.

.

INDUSTRIAL ELECTROCHEMISTRY

McGRAW-HILL CHEMICAL ENGINEERING SERIES

THE SERIES

INDUSTRIAL ELECTROCHEMISTRY

BY

C. L. MANTELL, Ph.D.

*Consulting Chemical Engineer, New York; Member, American Institute of
Mining and Metallurgical Engineers, American Institute of Chemical
Engineers; Chairman, Department of Chemical Engineering
Newark College of Engineering*

THIRD EDITION

INDUSTRIAL ELECTROCHEMISTRY

PREFACE

Electrochemistry has too often been given a minor place as a subdivision of physical chemistry, where it is frequently relegated to obscurity. The commercial importance and magnitude of those industries commonly classified as electrochemical are too little appreciated; the breadth, the scope, and the influence of these industries and their products on our daily life are too often unrecognized. Furthermore, the engineering side of the subject is neglected. Foreign technical literature, especially the German, abounds in texts and treatises on the industrial and engineering phases of electrochemical processes, while the American literature shows a paucity of book information on such topics. This volume endeavors to point out and emphasize the technological importance of electrochemical processes, to stress their practical aspects, and to adopt the engineering viewpoint.

The acceptance of the viewpoint expressed above by the author in the first edition, that electrochemical practice is a branch of chemical engineering and not a subdivision of physical chemistry, has been gratifying. This was further extended by a Spanish translation of the second edition.

The period since the preceding edition, which included the Second World War, brought forth tremendous expansion in the electrochemical and electroprocess industries, so that as a group they consumed more than a quarter of all power generated in the United States. New products and processes, an enormous increase in the size of cell and furnace units, and new sources of raw materials have made necessary considerable rearrangement of the text of this volume, as well as revision and inclusion of new matter. The engineering aspects have been given more attention.

Many friends who helped in previous editions have continued with advice, criticism of the manuscript, and in other intangible fashion. Permission to use certain illustrations and credit therefor is specifically acknowledged at various places in the text.

In reference to data, illustrations, viewpoint, and criticism on

salt electrolysis, C. C. Brumbaugh of the Diamond Alkali Company; U. Pomilio of Pomilio Corporation of Argentina; R. L. Murray and M. S. Kircher of the Hooker Electrochemical Company; E. E. Routh and W. C. Gardiner of the Mathieson Chemical Corporation; A. L. Carrad and F. Holt of the Imperial Chemical Industries; D. S. Dinsmoor, formerly of the Monsanto Chemical Company; B. M. Petrie of the Eastern Manufacturing Company at Bangor; C. W. Scheidler of the Great Western Electro-Chemical Company; F. G. Wheeler of Appleton, Wis.; H. M. Annis of the Oxford Paper Company; C. B. Barton of the Brown Company; N. Statham of the West Virginia Pulp and Paper Company; B. D. Millidge of the Howard Smith Paper Mills, Limited, at Cornwall, Ont.; J. H. Hubel of Canadian Industries, Limited, at Montreal; J. E. Plumstead of the Jessup & Moore Paper Company; L. D. Vorce of the Westvaco Chemical Corporation; on chlorates and perchlorates, J. C. Schumacher of the Western Electrochemical Company; on iron powder, B. T. duPont of Plastic Metals; on lithium, P. E. Landolt of the Lithium Corporation; on manganese, R. H. Bennett and E. M. Wanamaker of the Electro Manganese Corporation; on rectifiers, C. A. Escoffery and C. Smith of the Federal Telephone and Radio Corporation, all cheerfully cooperated.

The same is true for D. L. Ogden of The American Metal Company, Limited; E. R. Marble, H. Y. Walker, J. O. Betterton, S. H. Levison, and S. J. Dickinson of the American Smelting and Refining Company; J. H. Schloen of Canadian Copper Refiners, Limited; R. H. Waddington and O. B. J. Fraser of the International Nickel Company of Canada, Limited; J. P. Dyer and C. S. Harloff of the Phelps Dodge Refining Corporation; the Mount Lyell Mining and Railway Company, Limited; S. Skowronski of the International Smelting & Refining Company; O. B. Bennett of Rhokana Corporation, Limited; G. F. Creveling of the African Metals Corporation and the Société Générale Métallurgique de Hoboken in Belgium; H. Kingsmill and W. C. Smith of Cerro de Pasco Copper Corporation; F. Benard of the Ontario Refining Company, Limited; F. F. Colcord and F. S. Mulock of the U.S.S. Lead Refinery, Inc.; L. P. Davidson of the American Zinc Company of Illinois; P. F. McIntyre, B. A. Stimmel, and R. R. McNaughton of the Consolidated Mining and Smelting Company of Canada, Limited; W. C. Snow of the

Electrolytic Zinc Company of Australasia, Limited; A. Gronning-sater of Falconbridge Nickelverke; M. K. T. Reikie and J. D. Carr of the Hudson Bay Mining and Smelting Company, Limited; W. G. Woolf of the Sullivan Mining Company; C. M. Chapin, Jr., of the St. Joseph Lead Company; T. A. Campbell of the Andes Copper Mining Company; B. Wheeler and J. C. Allen of the Chile Exploration Company; F. Laist and R. B. Caples of the Anaconda Copper Mining Company; H. W. Aldrich, R. S. Newlin, and W. G. Scott of the Inspiration Consolidated Copper Company; J. Verdussen and A. Marthoz of Union Miniere du Haut-Katanga; S. V. Malcuit of the Aluminum Company of America; R. M. Hunter and W. R. Veazey of The Dow Chemical Company, in the various phases of electrowinning, electro-refining, fused electrolytes, and electrothermics; H. N. Blackmon, formerly of the Westinghouse Electric & Manufacturing Company, and H. H. Newton of the General Electric Company, in reference to power for electrochemical purposes; B. Kjellgren of The Brush Beryllium Company concerning beryllium; M. Eppley of the Eppley Laboratory in connection with standard cells; W. Blum and G. W. Vinal of the Bureau of Standards on primary and secondary cells; W. E. Holland of the Philadelphia Storage Battery Company and F. Brehme of the Edison Storage Battery Company concerning secondary cells; S. E. Sheppard of the Eastman Kodak Company on rubber deposition; E. Knowles of the International Electrolytic Plant Company, Limited, concerning hydrogen and oxygen cells; as well as S. D. Kirkpatrick, editor of *Chemical Engineering*, and H. C. Parmelee, editor emeritus of *Engineering and Mining Journal*, to whom the author is indebted for continuous advice.

As a result, the operating data approximate current practice, and obsolete practices are included only for historical interest or for the sake of rounding out the discussion.

It is a pleasure for the author· to acknowledge the help of R. N. Johnson, who prepared some of the charts; F. M. deSanta, who prepared copy; and Miss E. M. Rogers, who carefully prepared the manuscript and painstakingly corrected proof.

CONTENTS

ix

CHAPTER 1

SCOPE OF THE ELECTROCHEMICAL INDUSTRIES

Electrochemistry has been classically defined as the science which treats of the chemical changes produced by the electric current and the production of electricity from the energy of chemical reactions. Theoretically the two branches are of equal importance. Industrially, however, the chemical and physical changes produced by the use of the electric current are by far the more important.

Electrochemical engineering is a hybrid science having many ramifications. It may be considered primarily as a branch of chemical engineering upon which certain parts and aspects of electrical engineering and metallurgy have been grafted. Electrochemical engineering concerns itself, not only with all the topics generally considered as electrochemical, but also with the furnishing of power to the industries; the utilization of that power; the design, construction, and operation of the equipment, machinery, and plants employed to produce the electrochemical products; the economic considerations involved in the competition of chemical and electrochemical methods for the production of the same or similar products, as well as their sale, distribution, and consumption.

Electrochemical industries may be roughly divided into several classes: (1) those of an electrolytic nature, further subdivided into those of (a) the electroseparation type, represented by alkali and chlorine, (b) the electrowinning type, as represented by the copper and zinc industries in which the metals are produced by the leaching of ore, (c) the electrorefining group, of which electrolytic copper and nickel are examples, and (d) the electrodeposition type, represented by the electroplating and electroforming field; (2) the fused electrolyte group, represented by aluminum, magnesium, and the alkali metals as examples; (3) the electrothermal group, examples of which are calcium carbide, cyanamide, graphite, and the synthetic abrasives; (4) the

1

products of the electric furnace, which is used as a means of reaching elevated temperatures, such as the ferroalloys, electric steel, and special alloys; (5) the group which concerns itself with the conversion of chemical to electrical energy, as represented by the manufacture of batteries, of both the primary and secondary type; (6) a minor subdivision which, as the result of oxidation or reduction in electrolytic cells, is devoted to the production of inorganic and organic products; and (7) those industries in which the primary interest is concerned with the action of the electric current in effecting reactions and conversions in the gaseous phase. Each group and subdivision has problems and applications of the chemical and electrical engineering unit processes, but with the emphasis placed differently in the different groups.

The scope of the electrochemical engineering industries is very wide. The products are essential to our modern and everyday complex existence. To illustrate the breadth of the industries, a list of products of the electric furnace and electrolytic cell, at least as far as the major materials are concerned, is given. We will attempt in this volume to discuss these materials, their preparation, technical manufacture, and industrial properties, from the engineering viewpoint.

Electrochemical processes of an endothermic nature—*i.e.*, which take place with the absorption of electrical energy—have frequently supplanted purely chemical processes and in some cases allowed the production of new products which could hardly be obtained in any other way. Thus copper is now almost entirely refined by electrochemical means. All the chlorine used for water purification, sanitation, and bleaching is the product of electrolytic cells, while the manufacture of aluminum, calcium carbide, and the synthetic abrasives of the silicon carbide or fused-alumina type could not have reached their present commercial development without the use of electrochemical methods.

In chemical processes the necessary energy is ordinarily introduced as heat. It often happens that the simplest and most direct of the pure chemical methods for reaching certain ends cannot be used, owing to the great reaction resistances or the impossibility, under a given set of conditions, of converting thermal into chemical energy. As a result, it is frequently necessary to employ several successive reactions to replace a single direct

TABLE 1. PRODUCTS OF ELECTRIC FURNACE AND ELECTROLYTIC CELL

Product	Raw material	Electric furnace	Fused electrolyte	Electrolytic cell	Application
Alumina, fused	Bauxite (natural aluminum oxide)	x			Abrasives and refractories
Alumina, pure	Bauxite	x			Insulating material, aluminum metal
Aluminum, pure	Aluminum metal		x		Corrosion resistant coatings
Aluminum metal	Bauxite		x		Electric power transmission cable; lightweight alloys for airplanes, automobiles, and trucks; deoxidizing agent for steel; aluminothermic reactions; ammonal (explosives); acid containers; cooking utensils
Ammonium persulfate	Ammonium bisulfate solution			x	Oxidizing and bleaching agent, batteries
Anthraquinone	Oxidation of anthracene			x	Chemicals, dyestuffs
Antimony	Antimony ores			x	Alloying agent
Barium	Fused barium chloride		x		Alloys, electron emission
Beryllium	Beryl		x		Light alloys
Bismuth	Lead refining slimes			x	Alloys
Boron carbide	Anhydrous boric acid and coke	x			Abrasive
Cadmium	Zinc electrowinning slimes			x	Alloys, plating
Calcium	Calcium chloride		x		Special uses, radio tubes, lamps, alloys
Calcium carbide	Lime and coke	x			Acetylene for welding, cutting and lighting, acetone, acetic acid, airplane dope
Calcium cyanamide	Calcium carbide (nitrogen of the air)	x			Fertilizer, ammonia, cyanides
Carbon bisulfide	Coke and sulfur	x			Solvent, insecticide, carbon tetrachloride, artificial silk (viscose)
Caustic	Water, salt			x	Soap, paper industry, explosives
Cerium metals	Rare earth chlorides		x		Pyrophoric alloys, automatic lighters, tracer bullets and shells
Chlorine gas	Water, salt			x	Bleaching, gas warfare, mustard gas, phosgene, chlorpicrin, silicon tetrachloride, explosives, chlorbenzol, water purification, surgery (Dakin solution), detinning, artificial plastics, hydrochloric acid, aluminum chloride for oil refining, sanitation
Chrome yellow.. .	Lead			x	Paint pigment
Chromic acid.. .	Oxidation of chromium sulfate solution			x	Chromium plating, chemicals, oxidizing agent
Chromium.	Complex chromium ores			x	Alloying agent

TABLE 1.   PRODUCTS OF ELECTRIC FURNACE AND ELECTROLYTIC CELL—
(Continued)

Product	Raw material	Electric furnace	Fused electrolyte	Electrolytic cell	Application
Chromium	Chromic acid and sulfuric acid solution			x	Plating, alloys
Cobalt	Complex cobalt ores			x	Alloying agent
Copper, pure .	Copper ore			x	Electrical and brass industries
	Crude copper	.		x	
Cuprous oxide	Copper			x	Paint pigment
Deuterium	Water			x	Chemical for scientific use
Ferrochrome	Chrome ore	x			Special and high-speed steels, armor plate, projectiles
Ferrocolumbium	Residues from tin ores	x			Alloys, addition agents to steel, stainless steels
Ferromanganese	Manganese ore and coke	x			Steel, permanganates
Ferromolybdenum	Molybdenum ore	x			Special steels
Ferrosilicon	Iron, silica rock, coke	x			Making steel, making hydrogen
Ferrosilicon-titanium	Bauxite	x			Steel deoxidizer
Ferrotitanium .	Titanium ore	x			Scavenger in steel making
Ferrotungsten	Tungsten ore	x			Special and high-speed steels
Ferrovanadium	Iron vanadate	x			Special steels, automobile steels
Fluorine	Fused potassium acid fluoride or anhydrous HF		x		Chemical
Frary metal	Alkaline earth chlorides		x		Bearing alloys
Gold	Copper refining slimes			x	Jewelry, coinage, industrial alloys
Graphite	Coal and coke	x			Electrodes, lubricants, and paints
Hydrogen	Water, NaCH			x	Ballooning, hydrogenated fats
Hydrogen peroxide	Sulfuric acid solution			x	Chemicals, antiseptic, bleaching, oxidizing agent
Hypochlorite	Water, salt			x	Disinfectants, bleaches
Indium	Indium oxide in sulfuric acid solution			x	Nontarnishable silver alloy, jewelry, television
Iodoform	Alcohol, potassium iodide, sodium carbonate solution			x	Antiseptic, disinfectants
Iron, electrolytic .	Ferrous ammonium sulfate solution			x	Electromagnetic purposes
Iron, pig	Iron ore	x			Steel industry
Iron powder.	Iron ores or ferrous sulfate			x	Powder metallurgy
Iron, pure or "Swedish"	Pyrrhotite			x	Tubes and special steels
Lead, refined	Crude lead			x	Alloys, fittings, acid chambers
Lithium metal	Lepidolite, lithium salts		x		Light alloys
Magnesium metal . .	Magnesium chloride, sea water	:	x		Castings, sheet, cathodic protection anodes, lightweight alloys, flares
Manganese, electrolytic	Manganese ore			x	Ferrous and nonferrous alloys
Manganese dioxide ..	Manganese ore..		.	x	Depolarizer for dry batteries

TABLE 1.   PRODUCTS OF ELECTRIC FURNACE AND ELECTROLYTIC CELL—
(Continued)

Product	Raw material	Electric furnace	Fused electrolyte	Electrolytic cell	Application
Mannitol . .	Reduction of glucose solution			x	Esters, ethers, chemicals
Mercuric oxide . .	Mercury			x	Catalyst and chemical
Nickel, refined .	Crude nickel			x	Alloys, plating industry, dairy equipment, utensils
Nickel powder . .	Nickel			x	Powder metallurgy
Nitric acid .	Air	x			Explosives, fertilizers
Oxygen . . .	Water, NaOH			x	Oxywelding, oxycutting
Ozone	Air			x	Sterilization of water, sanitation
Palladium	Nickel refining slimes			x	Industrial alloys
Para-aminophenol .	Reduction of nitrobenzene			x	Chemicals, photographic developer, dyes
Perborates	Borax			x	Bleaching agents for textiles
Perchloric acid	Hydrochloric acid			x	Salts of perchloric acid
Phosphoric acid	Phosphate rock, coke, and sand	x			Acid phosphates, cleaners, food products
Phosphorus	Phosphate rock, coke, and sand	x			Matches, phosphorus compounds, phosphor bronze, smoke screens
Platinum	Nickel refining slimes			x	Catalysts, jewelry, industrial alloys
Potassium chlorate	Potassium chloride			x	Primers, matches, dyeing
Potassium hydroxide	Potassium chloride			x	Soap, chemicals, mercerizing cotton, electroplating
Potassium perchlorate	Sodium chlorate solution and converted to potassium salt			x	Oxidizing agent, explosives, medicine
Potassium persulfate	Potassium sulfate solution			x	Oxidizing agent, bleaching
Quartz, fused .	Quartz rock	x			Silica tubes, heat-resisting materials, optical uses, lenses
Rhodium	Nickel refining slimes			x	Industrial alloys
Rubber	Latex containing the usual components for compounding rubber			x	Household and industrial rubber goods
Silicon.. . . .	Sand and coke	x			Silicon steel, hydrogen for balloons, resistance units, silicides, silicon tetrachloride
Silicon carbide.	Sand, sawdust, and coke	x			Abrasives and refractories
Silver	Copper refining slimes			x	Jewelry, coinage, industrial alloys
Sodium bichromate	Chromium salts			x	Dyeing, tanning
Sodium chlorate	Sodium chloride solution			x	Weed killer, explosives, matches, oxidizing agent
Sodium metal......	Caustic (Castner); salt		x		Peroxides, cyanides, bleaching, mining
					Alloys, tetraethyl lead, organic synthesis
Sodium perchlorate.	Sodium salts, NaClO₃			x	Fireworks
Solder . . .	Impure tin-lead alloys			x	Metal joining

TABLE 1. PRODUCTS OF ELECTRIC FURNACE AND ELECTROLYTIC CELL—
(*Continued*)

Product	Raw material	Electric furnace	Fused electrolyte	Electrolytic cell	Application
Sorbitol	Reduction of glucose solution			x	Humectant, resins and plasticizers, vitamin C, chemicals
Tantalum	Potassium tantalum fluoride			x	Acid-resistant lining for chemical equipment
Thorium	Fused potassium thorium fluoride		x		Electron emission, X-ray targets
Tin, refined	Impure tin, tin dross			x	Tin-plate industry, bronzes
Tungsten	Sodium tungstate solution			x	Alloys, plating, electric bulbs
Uranium.	Fused potassium uranous fluoride		x		Alloys
White lead .	Lead			x	Paint pigment
Zinc, pure .	Zinc ore			x	Brass industry, galvanizing
Zinc powder .	Zinc			x	Powder metallurgy

one. Electrochemical processes usually involve the introduction of the needed energy, not in the thermal manner, but in an electrical one; or when the electric current is used for heating, it may be applied almost entirely at the point where it is desired. Usually the electrochemical processes are simpler and more direct than the corresponding chemical procedures. Sometimes, however, the electrochemical method is more expensive than its competitive purely chemical one but is preferably used, inasmuch as it allows the production of a purer product.

Electrochemical processes, however, cannot stand so much variation in their operation as chemical processes. Generally they operate satisfactorily only under constant conditions. It is therefore almost axiomatic that electrochemical processes should be as simple as possible. The raw materials used should be as pure as can be obtained or manufactured within the economic limitations of the process. Elimination of impurities is usually necessary so that side reactions introduced by the impurities may be prevented and efficiencies of operation maintained. The electrochemical industries for technical and economic success demand raw materials of ready availability and constancy of composition and supply. These are manufactured under constant and reproducible conditions into the desired products. If the raw materials for the operations be impure, preliminary chemical purifications are ordinarily warranted.

Commonly the electrochemical processes and industries dependent upon these need constant power supply, seldom interrupted, continuously available, and well regulated. In turn, electrochemical processes show high load factors of a steady and nonfluctuating nature. Usually for economic success cheap power is necessary. This factor is often so important that it is less expensive to bring the product to be treated to the source of power than to bring the power to the source of the raw material.

HISTORICAL DEVELOPMENT

At a dignified meeting of the Royal Society in London in the year 1807, Sir Humphry Davy lectured to a distinguished gathering on some of the chemical reactions caused by the electric current. Leaders of society paid a large admission fee to see the experiments. On the lecture table, mounted on a block of wood, there was a sheet of platinum with a wire connected to it. On top of the platinum was a stick of caustic with a small hollow filled with mercury. Another wire dipped into that. The wires were connected to a battery. The switch was closed, and after a while the mercury became stiff. Davy dropped the stiff mercury into water. It gave off hydrogen gas, which could be burned. He showed that the stiff mercury was an amalgam of mercury and sodium. By the action of the water and the amalgam a solution of caustic or lye was produced. In further experiments he produced globules of bright shining sodium metal and, in others, particles of the related metals, potassium, barium, strontium, calcium, and magnesium.

The setting, as far as the public is concerned, was the birthplace of electrochemistry. Great interest was aroused in Davy's work, and many prominent people subscribed to a fund to buy larger batteries. With these a few years later Davy showed electric arcs over an inch long. These were formed between pieces of charcoal or "poles." Davy spoke of the positive and negative poles, depending upon whether they were connected to the positive or negative side of his battery. Later Davy's assistant, Faraday, employed the word "electrode" as a general term for Davy's positive and negative poles.

It is a long cry from 1809 and the little black sticks of charcoal with which Sir Humphry Davy struck the first electric arc to the present day and the mammoth furnace electrode 15 ft long, 48 in. in diameter, and weighing nearly 9½ tons. Yet

these two sparking points are responsible, not only for the huge electrodes, but for the very furnaces in which they are used. They are the hub out of which in the next century our modern electrochemical products have come, through the medium of the electric furnace, the battery, the electrolytic cell, and modifications of these. The sparks from Davy's small electrode have had far-reaching effects. They have showered over so wide a territory that they cover one-tenth of all the chemical industries and represent hundreds of millions of dollars' worth of products a year.

The commercial development of the electrochemical industries, in their breadth and extent as we now know them, contributing to our present complex civilization is less than fifty years old, but the entire basic science and art go back little more than a century. This is strikingly illustrated in the march of progress depicted in Fig. 1.

Electrochemical processes require electrical energy, the existence of which was to all intents and purposes unknown before 1800 when Volta, an Italian nobleman, discovered that two unlike metals in contact with moistened paper or a salt solution gave a small electric current. A number of these couples in a pile was the first source of electrical energy used to break up water into its elements and provide for Davy's arc in 1807. Faraday discovered the inductive effects of the electromagnet, the basic principles for our electrical machines, as well as the underlying laws of the action of electrical energy on chemical substances and solutions. This was in 1834, a little over a hundred years ago.

Robert Hare of Philadelphia in 1816 invented his calorimotor, which was an electric battery for heating purposes. The chemical battery, invented by Daniell in 1836, furnished a new and more powerful source of electrical energy than did Volta's pile. In its wake and through its use came electroplating, so extensive today, developed by the Elkingtons in England from 1836 on; and electrotyping, the reproduction of articles, by Jacobi in 1839.   Wright in 1840 worked out the basis for plating solutions, little changed save in refinement of details, as used today.   Then came a lapse; but in 1849 we find cadmium plating discovered and rediscovered some seventy years later when commercial quantities of cadmium became available. Bunsen

separated magnesium metal from its salts in 1852 and lithium in 1855. The first did not find commercial favor until more than sixty years later, and the latter is still seeking its place in the metallurgical sun.

In 1859 there came a great step forward: Planté learned how to store electricity in his lead storage cell or secondary battery. Wöhler made calcium carbide in 1862. It was thirty years later, when trying to make aluminum, that Willson stumbled on it again, to start that present-day gigantic industry and the products made from it. In 1868 Leclanché made his cell or battery. This in modified form is the present-day dry cell, the foundation of a forty million dollar business producing an article of myriad applications. Adams commercialized nickel plating in 1869 and thus made possible the nickel-plated handle bar of the widely popular bicycle before the age of the automobile. Improvements in nickel plating introduced by Edward Weston in 1872 carried the art to a greater number of applications. C. M. Brush of Cleveland perfected his system of electric arc lighting in 1871. Batteries of a rugged nature allowed Robinson in 1871 to work out his method of train signaling, and Edison in 1874 the tremendous development of the quadruplex telegraph so that the same wire carried more than one message at a time.

Then began a new era of larger quantities of power. The electrical generating machine was built. In 1875 Anthony and Moler at Cornell University made the first American dynamo. By its use, Cornell's campus was lighted with electric lights while New York and Paris still used gas. In 1931 their dynamo was again operated as part of the Faraday centenary. Weston in 1874 had built a plating generator supplying a low-voltage current. Edison in 1879 produced the carbon-filament incandescent lamp and Brush the carbon-arc lamp. Both required power from sources of greater magnitude than batteries. "Central" stations so commonplace and readily accepted today were then developed. Bell's telephone in 1876 and the first telephone exchange in New Haven in 1878 could operate with batteries. In 1876 Carré, a Frenchman, had learned how to make carbon electrodes. In 1869 Elkington, from what had been done by his family in electroplating, learned how to purify copper commercially by electrochemical means, to produce a better material for carrying the electric current. Some four years later we find
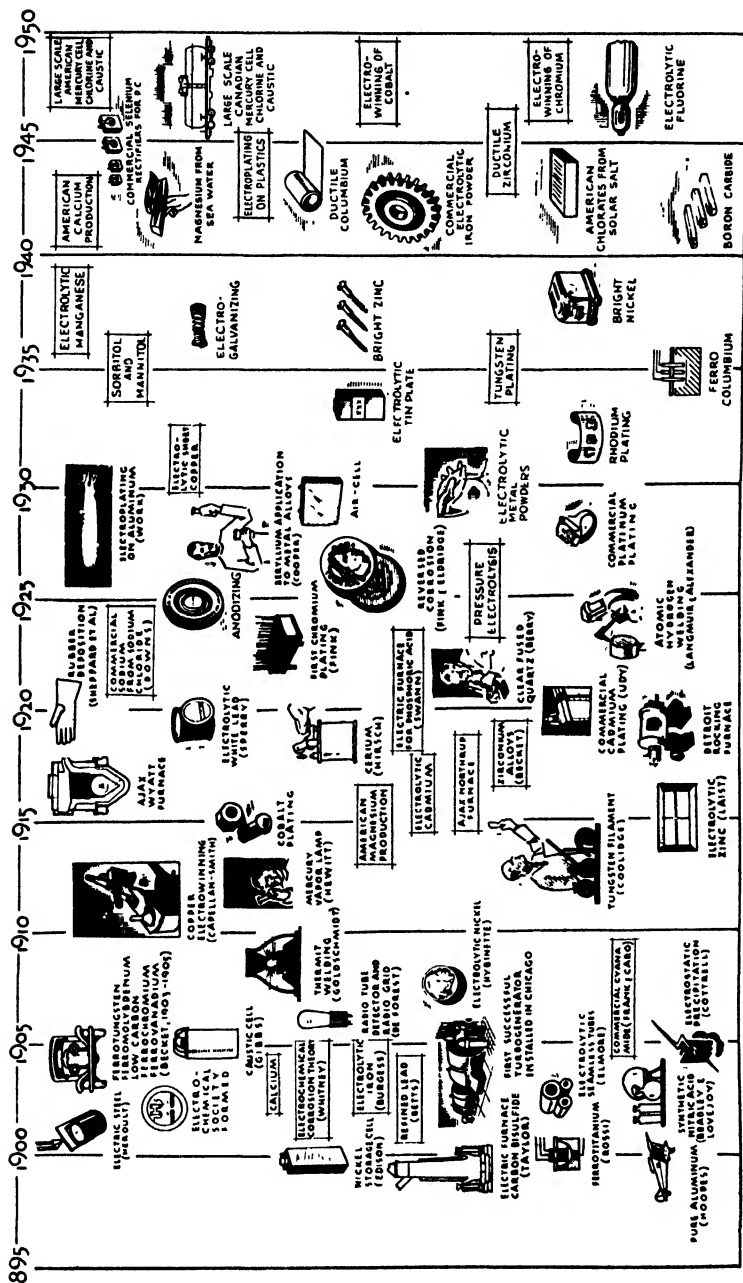
Fig. 1. March of progress of electrochemistry.

the Balbachs and the Thums producing electrolytic copper in the United States and working out mechanisms to refine silver.

The year 1882 brought forth a practical electric motor. Electrical machinery development moved apace, provided larger blocks of power, and the electrochemist was quick to follow with developments to use this power. Parsons' steam turbine in 1884 could drive larger dynamos more effectively. Bradley's rotary converter in 1887 was a forerunner of the present-day ease of transmitting alternating current and changing it to the required direct current.

Hall in 1885 worked out his aluminum process. T. L. Willson introduced the electric process for making calcium carbide in 1888, and the commercial manufacture of this material in an electric furnace was begun at Spray, N.C., in 1894. Gassner in 1888 had converted Leclanché's cell into its present-day dry form. Castner had also been searching for a way to make aluminum. He needed sodium metal to do it and in 1890 had invented a cheap method of making sodium metal, only to find his market had been taken by Hall's work. He also was the creator of the mercury-type alkali-chlorine cell, brought out in 1890 and operating today, producing the purest forms of caustic or sodium hydroxide. In 1891 Acheson, once Edison's assistant, while searching for a way to make diamonds in the electric furnace, hit upon silicon carbide, the first synthetic abrasive, which he called Carborundum. Tesla, another of Edison's coworkers, had made a motor driven by the alternating current.

There was then much talk about Niagara Falls. The stage was set for the most phenomenal of the electrochemical achievements. Electric furnaces and electrolytic cells were still in their infant stages but ready to grow up at a tremendous rate. Under the leadership of Adams, the power plants at Niagara Falls were begun and blossomed in 1894. Here was power in large quantities. The electrochemical industries needed cheap power day and night. They were invited to locate in Niagara, and a migration began.

But new industries did not cease to be born. In 1895 Moorehead made 50 per cent ferrosilicon. The blast furnace could not make ferroalloys of such high quality. From Acheson's Carborundum work an overheated furnace in 1896 gave him graphite. In the five years following, there came new ferroalloys which

could be made only in the electric furnace. The twentieth century was born but not before Jacobs had learned to melt aluminum oxide to bring forth a new, better, and stronger "emery," another abrasive which, with silicon carbide, was in two decades almost to wipe out the uses of many natural cutting materials.

In 1898 the Mathieson Alkali Works at Niagara Falls, N.Y., and the Dow Chemical Company at Midland, Mich., began the manufacture of bleaching powder from electrolytic chlorine. This was some six years after the General Electric Company had been established and some five years after E. A. LeSueur began the manufacture of caustic soda and bleaching powder by the electrolytic decomposition of sodium chloride at Rumford Falls, Me.

At the dawn of the century, Edison brought forth his nickel storage cell. Hoopes in 1900 outlined the steps for the manufacture of pure aluminum from Hall's product. A. J. Rossi had begun the smelting of titaniferous iron ores at Buffalo in 1894 and produced ferrotitanium in 1900. Shortly after the turn of the century, E. R. Taylor began the manufacture of carbon bisulfide in the electric furnace at Torrey, N.Y.

Conscious of the growing importance of the field, a group of leaders came together in 1902 to organize the American Electrochemical Society, which was to grow so international in scope that the term "American" was later dropped. One of these founders, Becket, two years later developed new and purer ferroalloys through the use of silicon instead of carbon. Whitney proposed the electrochemical theory of corrosion, a theoretical groundwork for the war against the toll of rusting and destruction by chemical and other agencies. Betts refined lead, Burgess iron, and Cottrell brought forth his method of electrostatic precipitation of dust and fume.

The year 1905 brought the cyanamide process of Frank and Caro, whose work is the basis of some of the nitrogen-fixation plants, as well as the basis of the peace-time uses of cyanamide, fertilizers, ammonia, cyanides, and urea.

Another field still young but growing at a tremendous rate was opened up by DeForest in 1906 with his radio-tube detector; mankind was beginning to train the ultimate energy particle, the electron, to do his bidding. Radio, television, talking motion

pictures, and all their ramifications were made possible, and the new field of electronics opened up to the world.   Hybinette in 1906 had worked out the kinks of commercial nickel refining. In 1907 F. G. Cottrell introduced the process for the electrical precipitation of suspended particles, a year after Baekeland's patents for regenerating electrolytes and for electrolytic diaphragms.

Then came a lull when faith was needed.   Chile had tremendous amounts of very low-grade copper deposits.   The Guggenheim organization backed the faith of Cappelan-Smith by spending millions to work out processes to win copper from ores of 1.5 per cent copper, lower than that thrown away by many mines, to emerge finally in 1912 as a tremendous development bringing forth the lowest production cost copper in the world, and making the electrochemist instead of the mining engineer the guiding hand.   Another new realm opened up—that of electrowinning—to be followed by Anaconda and others in 1915 applying related methods to zinc to produce a purer form than had been made before.   Two years later came commercial quantities of cadmium worked up from zinc by-products.   During this time there was great interest in the light metals, particularly in magnesium.   When produced in 1915, it was expensive, selling for over a dollar a pound; but it grew to an annual production by the Dow Chemical Company, from by-products of salt brines, of over a million pounds a year, to sell at one-fifth of its original price.

Electric furnaces of increased utility were manufactured, to find wider and wider application: the Ajax-Wyatt in 1916; Northrup's high-frequency furnace the same year; and before the First World War ended, the Detroit Rocking furnace so widely used in the nonferrous metal foundries of the United States.   In 1919 the electrochemist further invaded the strictly chemical field with the advent of electrolytic white lead.   The following year the Downs cell allowed the production of sodium from a cheaper material, salt instead of caustic.   The electric furnace was successfully applied to phosphoric acid in the same year, but further extension ·and expansion waited until 1934. The year 1921 brought renewed interest in coatings and platings —Sheppard and his coworkers learned how to plate rubber, an upside-down operation, for the rubber plated out at the positive

pole instead of at the negative one as with the metals. The next year Fink at Columbia University converted the laboratory method of chromium plating into a commercial process. In 1925 Fink learned the trick of reversing corrosion. Antiques thousands of years old were restored electrochemically. Berry in 1922 had applied the electric furnace to make clear fused quartz for mightier and more powerful optical instruments and telescopes. Langmuir and Alexander learned how to split the hydrogen molecule apart into its atoms, to let these recombine and thus make the basis of a powerful heating tool—the atomic hydrogen welding torch—in 1926.

Shortly afterward, the light metals, this time beryllium and lithium, commanded attention. Platinum was plated, followed by the use of rhodium in the same field in 1932. The introduction of the anodizing process for electrochemically treating aluminum occurred in 1925, and aluminum could be given many coatings and colors. Pressure electrolysis of hydrogen with the development of large capacity cells for doing this operation reached commercial application about the same time. In 1931 the copper producers commercialized electrolytic sheet copper, and, shortly after, electrolytic metal powders were produced in the refining tank. In the field of electroplating in rapid succession came tungsten as a coating in 1935, bright zinc in 1936, bright nickel in 1937, and electrogalvanizing from solutions similar to those employed in electrowinning in 1936. In the related field, electrolytic manganese was produced in the United States in 1939. Commercial processes were developed so that millions of pounds of pure metal were produced. Ferrocolumbium in 1935 was a new, useful ferroalloy, the same year in which sorbitol and mannitol were made by electrolytic oxidation-reduction processes from sugars. Plating methods have been developed and used commercially for almost every one of the metals in the periodic table. A large portion of the gold, more than half the silver, and almost all the platinum and rhodium are available through the working up of by-products from electrolytic copper, nickel, zinc, and to a smaller extent, lead. Secondary metals in a wide variety of mixtures are refined and their constituents recovered by electrolytic procedures. Alloy plating, electrolytic polishing, and "bright" coatings became of interest. Develop-

ment of high-speed strip steel as well as tin shortages focused attention on electrolytic tin plate, in which the coatings are applied at 250 to 1,000 fpm.

Just before and during the Second World War there came about a tremendous development of the electrochemical production of aluminum and magnesium where 40,000- and 50,000-amp cells became common, a vast hydroelectric power development with Hoover Dam and Boulder City, Bonneville and electrochemical plants in the Northwest, American production of calcium, larger chlorine cells and increased attention to those of the mercury type for pure caustic production, marked American expansion in chlorate manufacture, and the development of extensive fluorine chemistry with fluorine produced by electrolysis. Tremendous demands arose for electric furnace graphite for atomic-bomb manufacture.

During the Second World War period, intensive work was done on strategic metals resulting in electrowinning processes for antimony and electric furnace smelting of tin won by ore-dressing methods from complex ores of other metals. Pilot plants produced electrolytic cobalt and chromium by electrowinning. A wide variety of electrolytic metal powders were consumed as raw materials for the growing field of powder metallurgy. Some old battery systems were commercialized and new ones developed to satisfy demands for military purposes involving radio-directed signaling devices, radar, guided missiles, and other weapons.

Power for the electrochemical industries first depended upon the d.c. generator, then on the motor-generator set, then on the rotary converter. To these has been added the copper-oxide and selenium rectifiers as well as the mercury ignitron, large-capacity rectifier. The mechanisms all combine in providing efficient and flexible systems for power supply to the greatest power consumer which uses energy commonly 24 hr a day, and every day in the year—the electrochemical industries.

Part I

THEORETICAL ELECTROCHEMISTRY

CHAPTER 2

ELECTRICAL UNITS AND FARADAY'S LAWS

Electrical energy like other forms is a function of two factors: the quantity or current commonly expressed in amperes, and the intensity or potential difference ordinarily expressed in terms of volts. The extent of a change occurring in any energy content of a system is determined by both factors, but the possibility of a change is determined only by the intensity or the potential difference. In the well-known hydraulic analogy, water can move spontaneously from a higher to a lower level, the possibility depending upon the relative heights of the two levels. The potential energy change in such a system is the product of the weight of the water which has passed from one level to the other and the difference in height. Similarly, temperature difference is a thermal potential which will determine the possibility of heat transference, while affinity in a chemical reaction is a chemical potential. In such a system the product of the potential factor, or affinity of the reaction, and the quantity factor, or amount of matter which has been transformed, gives the quantity of chemical energy involved in the transference.

Electrical Units. The unit of electrical current strength is called the "ampere."[1] When electricity is passed through an aqueous solution of a metallic salt, the salt is decomposed. In many cases the metal is deposited in the free state. This phenomenon is a quantitative one. The ampere is defined as the unvarying electric current which will deposit silver at the rate of 0.00111800 g per sec from a solution of $AgNO_3$ in water under a given set of conditions.[2] The current density, commonly expressed in amperes or subdivisions or multiples of this unit per unit of cross-sectional area, is the current flowing through a

---

[1] Named after A. M. Ampère, (1775–1836), French physicist and chemist.

[2] It is specified that the $AgNO_3$ solution shall contain 15 to 20 g of salt to 100 g of distilled water. The solution must be used only once, not less than 100 cc at a time, and not more than 30 per cent of the metal must be deposited. The current density must not exceed 0.02 amp per cm² at the cathode, and 0.2 amp per cm² at the anode.

19

conductor divided by the area of the conductor. Common units are amperes per square foot or amperes per square decimeter.

In certain industrial operations, particularly in electroplating, current density may be the governing factor for the types of deposits desired. So-called "c.d. meters" are sometimes employed for control purposes in electroplating. These consist of cathode surfaces of definite area, connected in series with an ammeter, the mounting and connections being so arranged that the meter appears above the level of the bath and the whole apparatus can be hung on the cathode rod. The meter thus indicates amperes per unit of area.

The quantity of current is a function of both the current strength and time. The unit is the coulomb[3] or ampere-second, defined either as the quantity of electricity passing in one second at a current strength of one ampere, or, from the definition of the ampere, being that quantity of electricity which, when passed through a solution of $AgNO_3$, will deposit 0.00111800 g of silver.

The unit of electrical resistance is the ohm,[4] defined as the resistance of a column of mercury 106.3 cm in length with a cross section of 1 mm^2, at a temperature of 0°C.

The unit of the intensity factor, termed "electromotive force" or "potential difference," is the volt.[5] The volt of the International System of Electrical Units is "the electrical potential difference which, when steadily applied to a conductor having a resistance of one ohm, will produce in it a current of one ampere."[6] The volt cannot be easily produced as defined, owing to the definition of the ampere. The emf of a voltaic cell, however, can be determined against the international ohm and the international ampere, and such a cell can be used as a medium for realizing the international volt. "Standard cells" have provided the means for making comparisons of emf.

Standard Cells. The cells so used may be divided into two classes: primary standards, or normal cells, and secondary standards. The first are those by means of which the value of the volt is maintained, as at the Bureau of Standards or elsewhere.

---

[3] Named after C. A. Coulomb (1736–1806), French physicist.

[4] Named after G. S. Ohm (1787–1854), German physicist.

[5] Named after Count A. Volta (1745–1827), Italian physicist.

[6] "International Critical Tables," Vol. 1, p. 34, McGraw-Hill Book Company, Inc., New York, 1926.

The second are those suitable for general laboratory use. A system used as a primary standard should have an emf that is reproducible. In addition, such cells should be constant; their emf should not change with time, or, at the worst, should change slowly and according to a definite law. Secondary cells need not be reproducible, as they are calibrated against primary standards, although as a matter of convenience their values should fall within certain limits. They should be constant or show only slow and regular changes in emf.

Of all the cells formerly used or proposed, two systems only are of interest today; of these two but one is in general service. One pole is of pure mercury, overlaid with an excess of a sparingly soluble salt of mercury, Hg_2SO_4. The other pole is an amalgam of a metal more electropositive than mercury and covered with an excess of a soluble sulfate of the metal of the amalgam. The cell liquid is a saturated aqueous solution of this soluble salt of the amalgam metal.

As an excess of both Hg_2SO_4 and the sulfate of the amalgam metal is provided, the concentration of the solution with respect to these two salts when in equilibrium with them must be definite for every temperature within a range. Since the emf of the system is determined by the concentration of the solution, it will have a definite value for each temperature. This type of cell will be reproducible and is typical of the primary standard, or normal, cell.

If the solution be saturated at some temperature well below 4°C and the excess of the salt of the amalgam metal be omitted, a cell will result having a lower temperature coefficient than that of the normal standard. This form, known as the "unsaturated," cannot be held as reproducible, and is used as a secondary standard after calibration against a normal cell. Its lower temperature coefficient makes it desirable for general laboratory use.

The cell vessel is an H of glass tubing, the lower ends being closed and furnished with sealed-in platinum lead wires. It provides a long path between the electrode faces, thus reducing the effects of diffusion. Mercury and Hg_2SO_4 are placed in one limb, amalgam (with or without solid salt) in the other, and the vessel filled above the crossarm with solution. The upper ends are then sealed in the flame or closed with cork stoppers plus cement or wax.

When the metal of the amalgam is zinc and an excess of $ZnSO_4$ is present, the combination is known as the "Clark cell." It is reproducible and constant but has a high temperature coefficient. To fill the need for a standard with a lower temperature coefficient, giving greater accuracy in laboratory use, the Clark-Carhart cell was developed. This is the unsaturated type of Clark cell.

The Weston cell consists of an amalgam of cadmium, a solution of $CdSO_4$ having a concentration corresponding to that of a
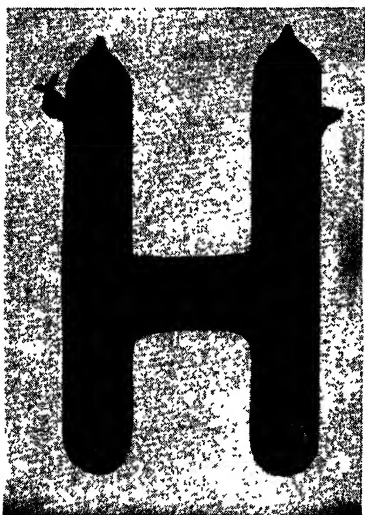
Fig. 2.   Weston standard cell.   (*The Eppley Laboratory.*)
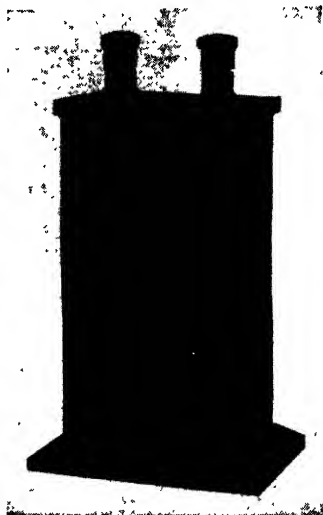
Fig. 3.   Commercial form of standard cell.   (*The Eppley Laboratory.*)

solution saturated at 4°C, and pure mercury overlaid with Hg_2SO_4. This combination has a very low temperature coefficient and is constant when properly made. It is not reproducible to the degree required in a primary standard. The "normal Weston" or "normal cadmium" cell, analogous to the Clark cell, having an excess of $CdSO_4$, is therefore the standard. Its emf is taken as 1.0183 volts at·20°C by international agreement. These cells are reproducible to better than 10 microvolts. Two typical forms are shown in Figs. 2 and 3.

A formula connecting temperature and emf between 0 and 40°C has been derived by Wolff and is accepted internationally.

It is

$$E_t = E_{20} - 0.00004075(t - 20) - 0.000000944(t - 20)^2$$
$$+ 0.0000000098(t - 20)^3$$

Relation of Electrical Units.   The relation between the quantity factor I and the intensity factor E is given by Ohm's law .

$$E = IR$$

or

$$I = \frac{E}{R}$$

wherein R is the resistance of the conductor.   The current strength is directly proportional to the emf and inversely proportional to the resistance.

The unit of electrical energy is the volt-coulomb or joule.[7] Since power represents the amount of energy per unit time, the unit of electrical energy is that power which will develop one joule per second.   This is known as the "volt-ampere or watt."[8]

The relation of the various electrical units is given in Table 2. Some of the quantitative relations existing between electrical and heat energy, which will be used in this book, are also included.

TABLE 2.   ELECTRICAL UNITS

Amperes $\times$ seconds = coulombs
Volts $\times$ coulombs   = joules
Volts $\times$ amperes   = watts
Watts $\times$ seconds   = joules
Kw = kilowatt = 1,000 watts
Watt-hour = 3,600 watt-seconds = 3,600 joules
Kwhr = kilowatt-hour = 1,000 watt-hours = 3,600,000 joules
Kw-yr = kilowatt-year = 8,760 kwhr = 31,536 $\times$ 10[6] joules
Hp = horsepower = 746 watts = 0.746 kw
Kw = 1 341 hp
1 joule = 0.2387 gram calorie (cal)
1 cal = 4.183 joules
1 kilogram calorie (Cal) = 4,183 joules
1 kwhr = 860.5 Cal = 3,415 Btu
1 hp-hr = 641.7 Cal = 2,547 Btu
1 Btu = 1,054 joules

Faraday's Laws.   Conductors of electricity may be sharply divided into three classes.   The first, the metallic or electronic

[7] Named after J. P. Joule (1818–1889), English experimenter.
[8] Named after James Watt (1736–1819), Scotch inventor.

conductors, consists of the metals, alloys, and a few other substances such as carbon. The current passes through these without the accompaniment of any ponderable quantity of matter. Those of the second class are termed "electrolytic conductors." They embrace in general the solutions of acids, bases, and salts, fused salts, some solid substances, and hot gases. In electrolytic conduction the movement of the current is always associated with a movement of matter. When the current leaves the electrolyte, it cannot take the matter with it; the latter is consequently set free. Chemical effects are produced. These mark the chief distinction between metallic or electronic and electrolytic conduction. In a third class with mixed conductors, the current passes partly in a metallic and partly in an electrolytic manner. Examples of these are the β form of silver sulfide and the solutions of the alkali and alkaline earth metals in liquid ammonia. By far the greater share of our attention in this volume will be devoted to the study of the chemical effects resulting from electrolytic conduction, and the corresponding electrical effects necessary for their production.

If two platinum plates or wires be dipped into a dilute solution of H_2SO_4 and connected either with two poles of a battery or with a source of direct current, electrolysis will take place. It will be noted that, at the platinum plate connected with the negative terminal of the battery, hydrogen gas is given off, while at the plate connected with the positive pole of the current source, oxygen is evolved. The gases are produced only at the platinum plates and not along the path of the current through the electrolyte. The plates are termed "electrodes," the negative pole being designated as the cathode and the positive one the anode. If we electrolyze a $AgNO_3$ solution, we will observe deposition of silver on the cathode and the evolution of oxygen at the anode. Whatever the solution, we note that chemical action takes place only at the electrodes, the points where the current enters and leaves the electrolyte.

The researches of Michael Faraday (1791–1867) led to the discovery of the quantitative relations between the amount of electricity which passes through a solution and the quantity of matter separated at the electrodes. The relations are expressed in the two laws named for him. The first states that the quantities of substances set free at the electrodes are directly propor-

tional to the quantity of electricity which passes through the solution. The second law expresses the fundamental relation between quantities of different substances liberated at the electrodes by the same quantity of electricity. It is: The same quantity of electricity sets free the same number of equivalents of substances at the electrodes. In other words, the quantity of silver liberated at the cathode by the passage of 20 coulombs of electricity through a solution of a silver salt is double that which would be obtained by the passage of 10 coulombs. The passage of the same quantity of electricity through solutions of a silver salt, a copper salt, an iron salt, a zinc salt, and an acid will set free quantities of silver, copper, iron, zinc, and hydrogen which are proportional to their equivalent weights.

To explain the phenomena, Faraday suggested that the neutral dissolved molecules of an electrolyte consist of two oppositely charged parts which he termed "ions," or wanderers. Those which move toward the cathode are called "cations," and those toward the anode "anions." When the current passes, the positive ions are attracted toward the negatively charged cathode, where their charge is neutralized and they are set free. In a similar manner, the anions move to, and are discharged at, the anode. This conception of Faraday's, developed in accordance with later discoveries, and the theory of electrolytic dissociation is now universally used.

The electrochemical equivalent of an element or a group of elements is the number of grams of that substance set free by the passage of one coulomb of electricity through an electrolyte. According to the laws of Faraday, electrochemical equivalents are proportional to chemical equivalents.

We have previously seen that one coulomb of electricity sets free 0.00111800 g of silver from a solution of a silver salt. If we divide the gram equivalent of silver (its atomic weight divided by its valence) by the electrochemical equivalent of silver, we find that

$$107.88 \div 0.00111800 = 96,494 \text{ coulombs}$$

This quantity of electricity is called a "faraday" (F). From the second law of electrolysis, if one faraday be passed through an electrolytic conductor, one equivalent of some substance will be liberated at each electrode. If $1F$ be passed through a solution

containing several electrolytes, the summation of the quantities of the different products set free at each electrode, when expressed in equivalents, will be unity.   Apparently there are no exceptions to Faraday's second law.   It is independent of the concentration of the electrolyte.   It holds good at all temperatures and for all solvents.   It holds for solid electrolytic conductors as well as for solutions and molten salts.   As a result of the large amount of investigation carried out to determine the exact value of the faraday, we find its value taken today to be 96,500 coulombs or 26.8 amp-hr.

Current Efficiency.   Although the minimum quantity of electricity needed for the production of a gram equivalent of a substance is 96,500 coulombs or 26.8 amp-hr, we find that in practice more than this amount is required.   That the actual quantity exceeds the theoretical is not due to the breakdown of Faraday's laws but to other causes.   There may be a separation of more than one substance at either electrode not taken into account.   The products of the electrolysis may suffer mechanical loss.   Secondary reactions may take place at the electrodes.   In addition there may be current leaks, short circuits, and losses in the form of heat.   The ratio of the theoretical to the actual quantity of current used is termed the "current efficiency."   In a similar manner, the actual amount of a product formed from a definite amount of current, divided by the theoretical amount, also gives us the current efficiency.   In commercial practice, current efficiencies may vary from as low as 25 to 30 per cent in the decomposition of certain fused salts and the electrodeposition of chromium from aqueous solutions of chromic acid, to as high as 92 to 95 per cent in copper refining, 95 to 98 per cent in certain electroplating applications, and 100 per cent in the electrolytic oxidation of anthracene to anthraquinone.

The current divided by the volume upon which the current acts is called the "current concentration."   If a high concentration is to be produced of some compound subject to chemical decomposition, a high value of this quantity is desirable.

Current Measurement.   Coulometers.   The determination of current efficiency involves the weight or volume of a product produced as the result of electrolysis and the quantity of electricity used.   The current may be measured by an ammeter at frequent intervals, when the average figure multiplied by the

time will give the number of ampere-hours expended. Galvanometers are used for the detection of the current and occasionally for the measurement of small amounts. Ammeters are generally employed for industrial purposes. Coulometers find application for the measurement of current in experimental work. Faraday's law is assumed, and all conditions are set so that 100 per cent efficiency is obtained in the instrument. The quantity of electrode product is weighed or measured directly or indirectly, and when divided by the electrochemical equivalent, the current in coulombs may be calculated. For satisfactory usage there must be no secondary reactions or disturbing influences in the coulometer system.

Coulometers are of several classes. In the weight coulometer the gain in weight of the cathode of an electric cell, due to the deposition of metal from a solution of its salt by the current, is measured. Volume coulometers are those in which the volume of a gas liberated as the result of electrolysis, or the volume of mercury set free during electrolysis of a suitable mercury salt, is measured. In titration coulometers the change in concentration or the amount of a substance set free at one of the electrodes is determined by analytical methods.

The errors of coulometers are those inherent in the measurement of weight and volume or in titration, and also those due to imperfections in the coulometer itself. The latter may come from a variety of causes, such as the liberation of substances other than the one assumed, or the loss of the substance after deposition and before weighing. The silver weight and the iodine titration coulometers are the most accurate, partly because of the high equivalent weights of iodine and silver.[9]

The silver coulometer has been the subject of a great deal of investigation, because on the accuracy of the measurement of quantities of electricity depend not only the value of the faraday and the definition of the ampere, but also the value of the emf of the normal Weston cell, which is employed as a universal standard of emf. The errors in the silver coulometer have been so completely eliminated that the results obtained for the emf of this cell by investigators in several countries, using three types of the coulometer, agree to about one part in one hundred thousand. For the specifications and supplementary notes of

[9] One gram Ag corresponds to 894.53, one gram I to 760.33 coulombs.

the silver coulometer, the reader is referred to the paper by Rosa and Vinal.[10]

For less accurate work the copper coulometer is often employed. The electrodes are of pure copper, the electrolyte consisting of 150 g of crystallized $CuSO_4$, 50 g of H_2SO_4 (sp gr 1.84), and 50 cc of ethyl alcohol[11] in 1,000 cc of distilled water. The strength of the current employed should not exceed 0.02 amp per cm^2 or fall below 0.002 amp per cm^2 of cathode surface. The anodes are best enclosed in bags of parchment paper to keep impurities from the electrolyte. The size of the coulometer is determined by the current it is designed to carry. When the electrolysis is finished, the cathode is withdrawn, washed thoroughly with water, then washed with alcohol, dried quickly, and weighed. Since the electrochemical equivalent of copper is 0.0003294, 1 g of copper deposited on the cathode of the coulometer corresponds to the passage of 3,040 coulombs of electricity through the electrolyte.

An example of volume coulometers is the water coulometer in which the volume of gas produced as the result of electrolysis of a 15 per cent solution of NaOH, NaCl free, between nickel electrodes is measured. The gases are collected and the volume measured at a definite temperature and pressure. Owing to the difficulties of collecting and accurately measuring large volumes of gas, this form of instrument is used only for the measurement of small quantities of electricity. Figure 4 shows a convenient form of the apparatus having a drying tube sealed to it.

$$1F \eqsim 1 \text{ g } H_2 \eqsim 11.2 \text{ liters } H_2 \eqsim 8 \text{ g } O_2 \eqsim 5.6 \text{ liters } O_2$$
$$\eqsim 16.8 \text{ liters } H_2 + O_2 \text{ at } 0°C \text{ and } 760 \text{ mm Hg}$$
$$\therefore 10.44 \text{ cc gas} \eqsim 1 \text{ amp-min}$$
$$\frac{10.44}{60} = 0.174 \text{ cc} \eqsim 1 \text{ coulomb}$$

The water coulometer is useful in the study of oxidation-reduction reactions. When connected in series with the electrolytic cell, a direct comparison may be made of the gases

---

[10] Rosa, E. B., and Vinal, G. W., *Bull. Bur. Standards*, **13**, 479 (1916); *Natl. Bur. Standards (U.S.) Sci. Paper* 285 (1916).

[11] The addition of ethyl alcohol to the solution minimizes the side reaction, $Cu^+ \rightarrow Cu^{++}$, at the surface of the electrolyte because of the absorption of oxygen from the air. The alcohol is slowly oxidized to acetone and acetic acid.

liberated in the oxidation-reduction cell and in the water coulometer. Indication is thus obtained of the current consumed in the oxidation-reduction reaction and that used in the formation of hydrogen and oxygen.

Washburn and Bates[12] proposed the iodine form of titration coulometer and stated that it was accurate with current density up to 0.5 amp per dm.[2] A platinum or a platinum-iridium electrode is set at the bottom of each limb of an H-shaped vessel. The anolyte, *i.e.*, the electrolyte around the anode, is concentrated potassium iodide solution; the catholyte is a solution of iodine in KI, with 10 per cent KI solution filling the rest of the vessel. As the result of electrolysis, iodine is liberated at the anode, dissolves in the potassium iodide, and is quantitatively determined with a standard sodium thiosulfate solution.

For less accurate work, the silver titration coulometer may be used. This type is accurate to within 0.1 per cent if the period of electrolysis be not more than 1 hr and the current strength not over 0.2 amp. The instrument consists of a tube 20 to 30 cm long and 20 mm in diameter, provided with a stopcock at the bottom. Into this casing and extending almost its entire length is inserted a small glass tube filled with mercury. A silver anode is sealed into the lower end, electrical connection being made through

Fig. 4.   Water coulometer.

the mercury. The outer tube is filled to about two-thirds its length with a 10 per cent solution of KNO_3, the remainder of the tube containing a 7 per cent solution of $Cu(NO_3)_2$ to which is added one-fifth of its volume of the KNO_3 solution. The cathode, a semicylindrical piece of platinum, dips into the upper solution. During electrolysis, one equivalent of silver per faraday dissolves from the anode. At the conclusion the solution is run off and the dissolved silver titrated by Volhard's method.
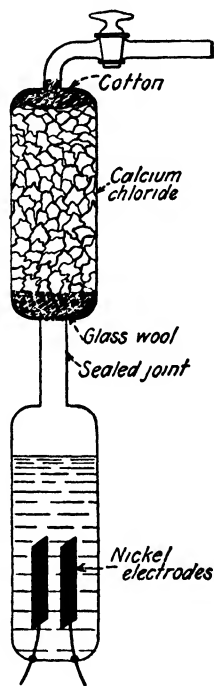
[12] WASHBURN, E. W., and BATES, S. J., *J. Am. Chem. Soc.*, **34**, 1341, 1515 (1912).

The Wright coulometer has been found satisfactory for rapid and exact measurement of electricity in industrial work. It consists of a glass vessel with a circular channel containing a mercury anode, the mercury being kept at a constant level by means of a connecting reservoir. A glass partition prevents the mercury from dropping into the lower part of the apparatus. The cathode of carbon is located immediately below the anode. The electrolyte used is a solution of potassium mercuric iodide. During electrolysis, drops of mercury are produced on the cathode. They do not adhere, but fall into a tube below, to which a scale is attached so that the volume of mercury may be read directly in ampere-hours. When the mercury rises to a point above the scale, the apparatus is inverted and the mercury allowed to flow back into the reservoir. The instrument is reliable within 1 per cent.

CHAPTER 3

ELECTROLYTIC DISSOCIATION AND CONDUCTANCE

In 1885 van't Hoff showed that for nonelectrolytes in solution the osmotic pressure is the same as its pressure would be if the dissolved substance were changed to a gas without decomposition and contained in the same volume as that occupied by the solution. In dilute solutions the gas law equation $PV = nRT$ applies to osmotic pressure.[1] For electrolytes, the calculation of P gives abnormal values, necessitating a correction factor and changing the expression to $PV = inRT$, where i, termed the van't Hoff factor, is always greater than unity and represents the deviation or abnormality.

Closely related to the osmotic pressure in solutions is the depression of the freezing point of a solvent produced by the presence of a solute. For nonelectrolytes such as sugar, alcohol, and urea the extent of this lowering is given by the expression[2]

$$\Delta = K \frac{n}{N}$$

The value becomes 1.858° for every formula weight of solute present in 1,000 g of water. Electrolytes, however, always give values which exceed 1.858, in some cases being two or more times this value.

Arrhenius Theory of Dissociation. In order to explain the behavior of electrolytes as far as the production of abnormal osmotic pressures and increased freezing-point depressions are concerned, Arrhenius in 1887 formulated a theory of electrolytic dissociation. It was assumed that the molecules of electrolytes break up into positively and negatively electrified particles or ions when dissolved in water. The abnormal osmotic effects

---

[1] P is the osmotic pressure, V the volume of the solution, n the number of mols in the solution, R the gas constant, and T the absolute temperature. $R = 0.0821$ liter atmosphere per deg, or 1.985 cal per deg.

[2] Δ is the lowering of the freezing point, K is a constant, and n is the number of formula weights of solute present in N formula weights of solvent.

produced by electrolysis may then be accounted for by the increase in the number of particles of solute present in a solution. The theory does not assume that all the molecules in solution are dissociated. If we represent the degree of dissociation of the fraction of each formula weight dissociated into ions by a and the number of ions into which each molecule dissociates by n, then

$$i = (1 - a) + na$$
$$= 1 + (n - 1)a$$

whence

$$a = \frac{i - 1}{n - 1}$$

By means of this equation, the degree of dissociation of an electrolyte may be calculated from osmotic pressure or freezing-point determinations.

Arrhenius's theory assumes that dissociation results in the formation of equivalent quantities of cations and anions, a conclusion resulting from the fact that solutions of electrolytes are always electrically neutral. The magnitude of the electrical charges carried by these ions may be calculated. We have previously seen that the passage of one faraday of electricity through a solution of an electrolyte liberates one gram equivalent of each ion or ions at each electrode. It follows that one gram equivalent of an anion is associated with 96,500 coulombs of negative electricity, and one gram equivalent of a cation with the same quantity of positive electricity. Accordingly, the quantity of electricity carried by any gram ion is nF, where n is the valence of the ion. One gram ion contains Avogadro's number of ions, which is 6.06×10^{23}. A single ion, therefore, must carry the charge equivalent to the amount carried by the gram ion divided by the number of ions present, or a simple multiple n of this quantity if the ion has a valence of more than 1. This ultimate quantity of negative electricity is called the "electron." It calculates to

$$\frac{96,500}{6.06 \times 10^{23}} = 1.59 \times 10^{-19} \text{ coulomb}$$

The chemical and electrical changes taking place during electrolysis may be expressed by electrochemical equations in which each faraday of positive electricity is indicated by a plus sign

($+$ or $\oplus$), and the corresponding amount of negative electricity by a minus sign ($-$ or $\ominus$). For example, the electrolysis of $CuSO_4$ in aqueous solution may be indicated

$$CuSO_4 \rightleftharpoons Cu^{++} + SO_4^{--}$$
$$\left.\begin{array}{l} Cu^{++} + \ominus = Cu^+ \\ Cu^+ + \ominus = Cu \end{array}\right\} \text{ at the cathode}$$
$$\left.\begin{array}{l} SO_4^{--} = SO_4 + 2\ominus \\ SO_4 + H_2O = H_2SO_4 + \frac{1}{2}O_2 \\ H_2SO_4 = 2H^+ + SO_4^{--} \end{array}\right\} \text{ at the anode}$$

or, summing up,
$$H_2O = 2H^+ + \frac{1}{2}O_2 + 2\ominus$$
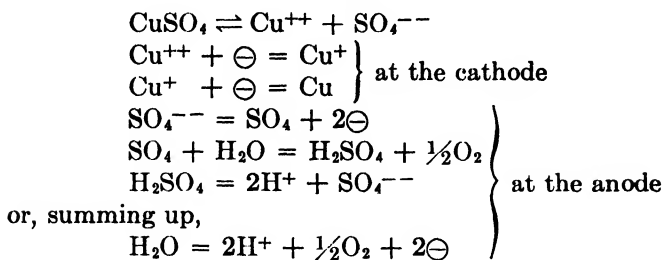
Solutions of electrolytes in solvents other than water conduct the electric current. It may be inferred that electrolytic dissociation takes place in these solvents. Substances which show conduction of the electric current in nonaqueous solutions are not necessarily dissociated in water. This solvent, however, is more effective in bringing about dissociation than most all others. Molten salts exhibit the same phenomena as solutions of electrolytes. It may therefore be concluded that ions are present in this type of electrolytic conductor.[3] In this portion of the subject, however, the theory has hardly advanced beyond the qualitative stage.

There is a rough proportionality existing between the dielectric constant of solvents and their dissociating power. Solvents with high dielectric constants, like water, possess a high dissociating power, while those of low dielectric constants dissociate dissolved material to a lesser degree. This follows from the fact that the attraction of electric charges for each other is inversely proportional to the dielectric constant of the surrounding medium.

Arrhenius's theory has survived more than half a century of experimental investigation and criticism, during which period it has contributed markedly to the progress of chemistry and physics. It has now, however, passed the stage of its triumphs and is faced by the problem of its difficulties and defects, some of which will be discussed later. It is generally agreed that the theory requires modification, although no case has yet been made out for its

[3] LORENZ, R., *Z. physik. Chem.*, **70**, 230 (1910); **79**, 63 (1912); MEYER, G., and HECK, A., *Z. Elektrochem.*, **28**, 21 (1922); *Z. physik. Chem.*, **100**, 316 (1922).

abandonment.[4]   Accordingly, in this book we shall adhere to the fundamental assumptions of the theory.   In a later section the newer modifications of electrolytic dissociation will be discussed. Arrhenius proposed incomplete breaking up of the molecules into ions.   The new theories are dependent upon the assumption that electrolytes are completely ionized and that the deviations from laws of perfect solutes are due to the electrostatic actions surrounding the ions and the interionic forces arising from the charges on the ions.

Ionic Mobility.   While Faraday's law indicates that the electric current is carried by the migration of ions, it states nothing about their relative or absolute velocity of movement.   Hittorf[5] has shown that the relative ionic velocity can be determined from the concentration changes that take place at the electrodes. Let us suppose we have an electrolytic cell containing a solution of HCl, so that we have 30 gram atoms of hydrogen ions and an equal number of chlorine ions.   Let the cell be divided into three equal parts by two porous diaphragms placed between the electrodes, the diaphragms serving merely to prevent mechanical mixing without interference with the passage of the current.   If we allow $6 F$ of electricity to pass through the cell, six equivalents of hydrogen will be deposited on the cathode and six of chlorine at the anode.   If the hydrogen and chlorine ions move at the same rate and if nothing takes place at the anode or cathode beyond the mere discharge of ions, the concentration changes produced at the electrodes will be identical.   On the contrary, suppose that the oppositely charged ions move at different rates. If the current were carried entirely by positive ions, during the time the six equivalents were deposited on the electrodes, six equivalents of positive ions would pass every section of the cell.

The concentration of HCl in the cathode compartment would remain unchanged, since all six positive ions liberated were replaced by migration of six others and no negative ions were lost. At the anode, however, deposition caused the loss of six negative ions and migration the loss of six positive ones, so that the concentration of the solution in this area was diminished by six equivalents of HCl.

If, as is actually the case, the hydrogen ions move five times as

[4] KENDALL, J., *J. Am. Chem. Soc.*, **44**, 737 (1922).
[5] HITTORF, W., *Pogg. Ann.*, **89, 98, 103, 106**, (1853–1859).

rapidly as the chlorine ions, then five equivalents of hydrogen will cross each section of the cell toward the right, while one of chlorine passes to the left. In ·the cathode compartment six equivalents of hydrogen are deposited but only five migrate in. One equivalent of chlorine is lost by migration, and the cathode compartment therefore loses one equivalent of HCl. In a similar manner it can be shown that the anode loses five equivalents. The following relations then hold:

$$\frac{\text{Velocity of cation}}{\text{Velocity of anion}} = \frac{U_c}{U_a} = \frac{\text{loss in equivalents at anode}}{\text{loss in equivalents at cathode}}$$
$$= \frac{\text{equivalents of cation transferred to cathode}}{\text{equivalents of anion transferred to anode}}$$

From this it follows by proportion that

$$\frac{U_c}{U_c + U_a} = \frac{\text{equivalents of cation transferred to cathode}}{\text{total equivalents of ions transferred in both directions}}$$

This fraction is called the "transference number" or "transport ratio" of the cation n_c, and $U_a/(U_a + U_c) = n_a$ is the transference number of the anion. Evidently $n_c + n_a = 1$; *i.e.*, the sum of the equivalents of positive and negative ions that cross any section of the electrolyte when 1 F passes equals unity. The same considerations apply to polyvalent ions.

The transference number of an ion in a given electrolyte thus represents the fraction of the total current carried by that species of ion during electrolysis. The ratios of the transference numbers of the anions and cations are equal under the given conditions to the ratio of their respective mobilities.

By the employment of suitable apparatus and the observing of precautions to minimize the disturbing effects of diffusion and mixing, it is possible to measure the extent of concentration changes which occur in the neighborhood of one of the electrodes during electrolysis. If the total current of electricity passed through the cell be measured by a coulometer, the transference numbers of the ions in the electrolyte can be determined.[6]

[6] For the exact methods of determining transference numbers and a description of the apparatus, with discussions of their accuracy and the necessary precautions to be taken, the reader is referred to the standard works on physical chemistry and physicochemical measurements.

Transference numbers seldom have any direct bearing on electrochemical processes in practice. Concentration changes may result near the electrodes, partly due to unequal rates of migration if electrolysis take place in a solution not in motion. Such concentration differences are undesirable in that they increase the voltage required by the cell and may lead to the production of impure products at the electrodes. Concentration changes are thus as far as possible destroyed by continuous circulation of the electrolyte or mechanical mixing. Hence calculations involving transference numbers usually do not find industrial application.

Conductance. In any industrial cell in which electrolysis is taking place, it is obvious that there are ohmic resistances in various portions of the system which cause loss of energy and the liberation of heat. At contacts, connections, and joints there will be contact drops whose importance becomes large or small depending upon the care given to them. Obviously the electrolyte is a conductor in the system, not perfect in nature, and shows ohmic resistance. The electrolyte, however, differs from metallic conductors in that the passage of current through the electrolyte causes chemical effects at the electrodes which are the contact points or areas in the circuit.

For a conductor of uniform cross section throughout its length, the resistance is a direct function of the length and an inverse function of the cross section represented by the equation[7]

$$R = r \frac{l}{a}$$

If l be 1 cm and a 1 cm², the resulting value of resistance expressed in ohms per centimeter cube is the specific resistance r. From the expression above,

$$r = \frac{aR}{l}$$

In the English system, l would be 1 in. and a 1 in. sq. and the specific resistance would be ohms per inch cube.

Conductivity is the reciprocal of resistance, and specific conductivity κ bears the same relation to specific resistance and equals l/Ra. Inasmuch as from Ohm's law $E = IR$, where E is electromotive force or voltage, I is the current, and R is the

---

[7] l is the length, a the cross-section area, r the specific resistance, and R the total resistance.

resistance, and $R = E/I$ and $1/R = I/E$, the specific conductivity κ equals Il/Ea and is equal to the current flowing across the centimeter cube of the electrolyte at a potential of one volt.

The conductivity of a solution depends upon the electrolyte and its nature, the solvent, the concentration, and the temperature. Specific conductivity increases with concentration to a maximum, after which the specific conductivity decreases. The specific conductivity-temperature relation is almost linear, following the expression

$$\kappa_t = \kappa_{18}[1 + b(t - 18)]$$

where b has values of 0.02 to 0.025 for salts and bases and 0.01 to 0.016 for acids. According to Noyes,[8] the relation is good over a temperature range including those considerably above 100°C. Little attention shall be devoted in this book to the experimental methods for determining specific conductivity of electrolytes, inasmuch as the matter is treated in considerable detail in the textbooks of practical physical chemistry.

The factor "equivalent conductivity" is of somewhat wider use in the study of the question of electrolytes than is specific conductivity. The symbol for equivalent conductivity is Λ and is defined by the relation

$$\Lambda = \kappa v$$

where κ is the specific conductivity of the solution and v the volume of the solution containing 1 gram equivalent of the solute. Apparently volume is the important factor in the determination of equivalent conductivity, since Λ is directly proportional to v. Furthermore, the specific conductivity κ decreases with increased volume except in very strong solutions. Actually, the work of Kohlrausch and others has shown that the equivalent conductivity increases with the dilution of the electrolyte. At first the change in value is rapid, gradually diminishing until, at sufficiently high dilutions, a maximum which is practically constant is reached. Solutions may become too dilute for the measurement of this limiting value. This maximum which Λ approaches is called the "equivalent conductivity" at infinite dilution, and carries the symbol Λ_∞.

Kohlrausch, in his studies of various electrolytes, showed that

[8] Noyes, W. A., *Carnegie Repts.*, **63**, 340 (1907); *cf.* Walden, P., and Ulich, H., *Z. physik. Chem.*, **106**, 49 (1923).

the equivalent conductivities at infinite dilution may be considered as of two parts. One of these is characteristic of the anion, the other of the cation. Hence the value may be expressed by

$$\Lambda = l_a + l_c$$

where l_a and l_c are quantities governed by the types of anions and cations, respectively, termed the equivalent ionic conductivities of the ions under study.

When a sufficiently large emf is applied to two electrodes immersed in a solution of an electrolyte, all the ions present start to move. This movement of ions constitutes the flow of electricity through the electrolytic conductor. When the source of the emf is an electrical machine, electrons flow from its negative side along a connecting wire to the cathode. The electrons are acquired by the positive ions which thus become neutral atoms at the cathode. Simultaneously, the negative ions are discharged by their loss of an electron at the anode. These electrons then return along the conducting wire to the positive side of the electrical machine. This exchange of electrons constitutes an electrochemical reaction. For example, if a solution of $AgNO_3$ be electrolyzed between silver electrodes, the silver ions each take up an electron from the cathode, depositing on this electrode as neutral atoms:

$$Ag^+ + \ominus = Ag$$
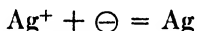
At the anode silver enters the solution as ions. The reactions occurring at the anode may be expressed as follows:

$$NO_3^- = NO_3 + \ominus$$
$$Ag + NO_3 = Ag^+ + NO_3^-$$

or

$$Ag = Ag^+ + \ominus$$
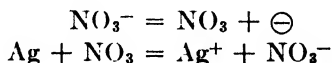
Each neutral silver atom of the anode loses an electron, entering the solution with a single positive charge as an ion. Through this electrolysis, therefore, one gram ion of silver is discharged at the cathode and an equivalent quantity of this ion is formed at the anode for every faraday of electricity passing through the solution.

Suppose a cell be constructed which is a cube 1 cm in every dimension. Two opposite faces of the cube are made of platinum

to act as electrodes, the bottom and two other faces being of glass. If a potential of 1 volt be applied, the current which flows will be a function of the specific conductivity of the electrolyte. Suppose a simple salt, BA, which gives the ions B^+ and A^-, be in a solution containing 1 gram mol of BA in v cc, then α = per cent dissociation of BA at concentration 1 gram mol in v cc. Let $F = 96,500$ coulombs, u_a = velocity of the anion in centimeters per second under 1 volt per cm, u_c = velocity of the cation in centimeters per second under 1 volt per cm. Let κ = specific conductivity, Λ = equivalent conductivity, and $\Lambda = \kappa v$, then the anions per centimeter cube = cations per centimeter cube = α/v gram equivalents. The charge on the anions = the charge on the cations = $F(\alpha/v)$. Energy carried by the anions per second equals

$$\frac{F\alpha}{v}\,u_a$$

and for the cations

$$\frac{F\alpha}{v}\,u_c$$

the sum of which is

$$\frac{F\alpha}{v}\,(u_a + u_c) = \kappa$$

Since $\Lambda = \kappa v$,

$$\Lambda = F\alpha(u_a + u_c)$$

Λ varies thus with α, the ionization, and with u_a and u_c, which are the ionic velocities. With dilution α approaches unity as a limit so that at infinite dilution

$$\Lambda_\infty = F(u_{a_\infty} + u_{c_\infty})$$

If the assumption be made that ionic velocities or mobilities are not dependent on concentration, then

$$\Lambda_\infty = F(u_a + u_c)$$

and the relation between equivalent conductivity at finite dilution v and at infinite dilution becomes

$$\frac{\Lambda_r}{\Lambda_\infty} = \frac{F\alpha(u_a + u_c)}{F(u_a + u_c)} = \alpha$$

Equivalent conductivities are given in Table 3 for a number of inorganic acids, bases, and salts, including examples of those

which are often referred to by the chemist as weak, moderately strong, and strong electrolytes. Where lower values are not given, the values for the concentrations of $0.001N$ are in many cases equal to, or approximately the same as, the conductivity at infinite dilution, *viz.*, Λ_∞, so that α values or percentages of ionization may be calculated from the table. When conductivity values in the table in terms of reciprocal ohms or mhos are given for concentrations lower than $0.001N$, *e.g.*, $0.0001N$, these values may be taken as the approximate conductivity at infinite dilution or Λ_∞ for that particular solute.

The resistance of electrolytes at various concentrations may also be calculated from the figures given in the tables from the relationship between conductivity at finite dilution Λ_v, the specific conductivity κ, and the volume v containing 1 gram equivalent of the solute, in that

$$\Lambda_v = \kappa V$$

and

$$\kappa = \frac{1}{r}$$

where r is specific resistance. Thus

$$\Lambda_v = \frac{V}{r}$$

and

$$r = \frac{V}{\Lambda_v}$$

It is obvious that the normalities can be converted into V or volumes containing 1 gram equivalent. If the normalities are multiplied by 10^3, concentrations C in milliequivalents per liter may be substituted in the expression

$$\Lambda_v = \frac{10^6\kappa}{C}$$

and these results employed for the calculation of specific conductivities and resistances.

The values in Table 3 have been taken from the more extensive tables of Washburn and Klemenc and Parker and Klemenc in Vol. VI of the "International Critical Tables" of the National

Research Council and published by the McGraw-Hill Book Company, Inc., by permission. In the table, unless otherwise stated, the values are at 18°C, so that calculations based upon the figures given in this table must take this temperature into account.

Mass Action and Dilution Law. According to the Arrhenius theory, an electrolyte should contain undissociated molecules and ions existing together in equilibrium. If the equilibrium be represented as

$$M_zA_y \rightleftharpoons xM + yA$$
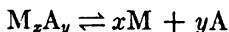
the application of the law of mass action should give

$$\frac{(M)^z(A)^y}{M_zA_y} = K$$

where K is a constant at constant temperature. The active mass of a constituent may be regarded as its concentration in gram molecules per unit volume of solution. In a simple electrolyte such as MA, if the concentration of the original salt be 1 gram molecule in v liters of solution and the degree of dissociation be α, then the concentrations of MA, M^+, and A^- will be $(1 - \alpha)/v$ and α/v for each of the metal and acid ions. Applying the law of mass action, the expression becomes

$$\frac{\alpha^2}{(1 - \alpha)v} = K$$

The relation given in this expression is known as the "Ostwald dilution law." This law holds accurately over a wide range of concentration for weak electrolytes but is quite inapplicable for strong electrolytes.

At extreme dilutions, however, the dilution law may be applied to any electrolyte. It is of considerable use in the case of the solubility of sparingly soluble salts. Thus in the case of AgCl we have the equilibria

$$AgCl_{solid} \rightleftharpoons AgCl_{dissolved}$$
$$AgCl_{dissolved} \rightleftharpoons Ag^+ + Cl^-$$
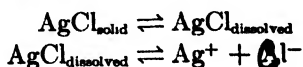
Inasmuch as the salt is only very slightly soluble, its concentration must therefore be very small, or its dilution may be considered to have reached that point at which 100 per cent ion-

TABLE 3.   EQUIVALENT CONDUCTIVITIES OF SALTS, ACIDS, AND BASES
(Mhos)

Compound	°C	0.0001N	0.0005N	0.001N	0.01N	0.1N	0.2N	0.5N	1N	2N	3N	4N	5N	6N	7N	10N	20N	Reference
AgNO₃		114.85	113.72	113 0	107 62	94.2	87.8	77 3	67 5	55.9	48 4	42.3							(1, 2, 3)
Ag₂SO₄				116 8	103.3			65 0	56.2	44.5	34.2	27.1							(4, 5)
AlCl₃	25			125.	108	87.9	80.5	69 6											(1)
Al(NO₃)₃	25			107 0	67 3														(6)
Al₂(SO₄)₃					108														(7)
BaCl₂		115.16	116 85	115 44	106 82	90 65	85 23	77 18	67 45	58.0	49.7	42 4	35 6						(2, 8)
Ba(NO₃)₂		115.01	113 14	111 8	106 82	78 83	70 05	56 52	55 79	42.7	33.5	26.5		14 2		23.5			(2, 3, 9)
CaCl₂		111 75	113 18	111 8	100 82	88 07	68 69	74 61	53.9	14.1	10.4	24	4 8	13.7	3.	5			(2)
Ca(NO₃)₂			109 78	108 34	99 39	82 37	75 54	65 61	23 56	17.9	14.	10 8	18 4		11.	1 2			(2, 10)
CdCl₂				104 8	92 9	50 0	41	23 4	60 8	49.2	40.8	32 1	8.2		12.				(11, 12, 13)
Cd(NO₃)₂		109.69	102 79	109 2	92 9	79 0	73 5	28 7	58 0	46.8	37 6	29 9	23.3						(12, 13)
CdSO₄				97 58	70.23	42 15	35 84												(2, 12)
CoCl₂								66 2	58 3	43 2	33 3	25 5	19.						(1, 14)
Co(NO₃)₂						51 4	43 9	33 3	58 0	43 2	33 3	25				4 6			(1)
CoSO₄	25			113.4	82 5	82 2	74 1	64 8	55 9	45 5	36 2	26 0							(6)
Cr(NO₃)₂					108.6	83 2	77 1	67 2	57 9	45	36 2	28 4							(1, 15)
CuCl₂						81 9	76 6	67 2	57 57	48.5	37								(8, 16)
Cu(NO₃)₂		109 80	103.42	98.42	71 64	43.8	37 6	30 7	25 74	20.	25 7	30 8	24 0	19 1		4 6			(16)
CuSO₄								69 4	60 6	48.1	38 8	20 9	15.9	12 4					(2, 10)
FeCl₂								64 5	58 1	37.5	27 8	11.9							(1)
FeCl₃								30 8	23 8	19 5	15 3	28 5							(1)
FeSO₄								75 0	63 8	48.5	37 5								(17)
Fe(NO₃)₃					1 5														(1)
HgCl₂				2 6		1 98	17 69	05 05	101 2	95 5	91 9	86 9	24 0	13 1		11.3			(12)
KBr		130 86	129.86	129 1	124 13	113 98	110 17	105 05	101 2	95 5	91 9	86 9							(8, 18, 19, 20, 21)
KCl		128 83	127.86	127 122	122 18	111 79	107 74	102 25	98 03	98 08	88.1								(22, 23, 24)
KClO₃		118 45	117.50	116 7	111 5	99 0	93 6												(21, 25)
KF		110 02	109 03	109 45	103.85	93 63	89 1	82	75 7	66 0	58 9	52.7	46.9	42.0					(9, 16, 26)
KNO₃		125 2	124 16	123 37	117 93	104 56	98 53	89 12	80 33	69 0	61 3								(9, 22, 25)
K₂SO₄		130.5	128.3	126 7	115.6	94 8	87 8	73 1	71 5										(2, 3, 9, 17, 27)
LiBr						84 3	80 8	71 5	67 2	57 7	50 5	44.2							(19)
LiCl		97 82	96 87	96 2	91 84	82.76	77 69	70 5	63 18	53 0	45 2			33.3					(22)
LiNO₃		94.17	93 23	92 58	88 33	78 95	74 79	67 61	60 61										(9, 22)
MgCl₂	0				65 7	55 2	51 8	46 0	40 6	33 0	27	32 1	8 8	16.3					(6, 28, 29, 30, 31)
Mg(NO₃)₂	0						57	67 2	59 5	47 9	39 2	12 0	21 6						(5, 8, 9)
MgSO₄		109.6	104 2	102 5	94 52	80 4	75 2	64 4	28 99	21 4	16 1	45 3	8 8						(2, 3, 32, 33)
MnCl₂				99.9	76 0	49 57	43 0	66 8	58 9	47 5	37 9	30 3	23 5						(1)
Mn(NO₃)₂																			

Substance		References
MnSO₄		(17)
Na₂B₄O₇		(34)
NaBr		(19)
NaCl		(22)
NaClO₃		(8, 16, 35)
Na₂CO₃		(36, 37)
Na₂C₂O₄		(16, 38)
NaF		(9, 21)
NaNO₃		(8, 9, 22)
Na₃PO₄		(34)
Na₂SO₄		(1, 2, 9, 17, 20, 26, 27, 36, 37)
NH₄F		(16)
NiCl₂		(1)
Ni(NO₃)₂		(10, 17, 39, 40)
NiSO₄		(5, 9)
PbCl₂		(2, 9, 41)
Pb(NO₃)₂		(2, 29, 30, 31)
SrCl₂		(2, 9)
Sr(NO₃)₂		(16, 41)
ZnCl₂		(16)
Zn(NO₃)₂		(2, 10)
ZnSO₄		
Acids:		
HBr		(16)
HCl		(10, 37, 42, 43, 44)
HCl		(59, 60, 61)
HClO₃		(8, 16, 19)
HClO₄		(46, 47, 48)
H₂C₂O₄		(7)
HNO₃		(10, 31, 42, 49, 50)
H₃PO₄		(49)
H₂SO₄		(51)
H₂SO₄		(5, 49, 52, 53, 54)
Bases:		
Ba(OH)₂		(36, 49)
Ca(OH)₂		(47)
KOH		(36, 37, 55)
LiOH		(8, 16, 19)
NaOH		(36, 37, 55, 56, 57, 58)

ization of the salt occurs. It therefore follows that in the mass action equation the concentration of the un-ionized AgCl is negligible in the solution and the term may be dropped from the equation. Thus we can deduce the relations

$$\frac{(\text{AgCl}_{\text{dissolved}})}{(\text{AgCl}_{\text{solid}})} = k_1$$

$$\frac{(\text{Ag}^+)(\text{Cl}^-)}{(\text{AgCl}_{\text{dissolved}})} = k_2$$

[1] HEYDWEILLER, *Z. anorg. allgem. Chem.*, **116**, 42 (1921).
[2] KOHLRAUSCH and GRÜNEISEN, *Sitzber. preuss. Akad. Wiss.* (1904), p. 1215.
[3] NOYES and MELCHER, *Carnegie Inst. Wash. Pub. No.* 63, 71 (1907).
[4] DRUCKER, *Z. physik. Chem.*, **96**, 381 (1920).
[5] HUNT, *J. Am. Chem. Soc.*, **33**, 795 (1911).
[6] JONES, *et al.*, *Carnegie Inst. Wash. Pub. No.* 170 (1912).
[7] WALDEN, *Z. physik. Chem.*, **2**, 49 (1888).
[8] CLAUSEN, *Ann. Physik*, **37**, 51 (1912).
[9] NOYES and FALK, *J. Am. Chem. Soc.*, **34**, 454 (1912).
[10] KOHLRAUSCH and HOLBORN, "Das Leitvermogen der Elektrolyte," Teubner, Leipzig, 1916.
[11] GROTRIAN, *Ann. Physik Chem.*, **151**, 378 (1874).
[12] GROTRIAN, *Ann. Physik Chem.*, **18**, 177 (1883).
[13] WERSHOVEN, *Z. physik. Chem.*, **5**, 481 (1890).
[14] MAZZETTI, *Gazz. chim. ital.*, **54**, 891 (1924).
[15] BJERRUM, *Z. physik. Chem.*, **59**, 336 (1907).
[16] HEYDWEILLER, *Ann. Physik*, **37**, 739 (1912).
[17] KLEIN, *Ann. Physik Chem.*, **27**, 151 (1886).
[18] GROPP, Dissertation, Rostock (1915).
[19] HEYDWEILLER, *Ann. Physik*, **30**, 873 (1909).
[20] HEYDWEILLER, "Gesammelte." Abhandlungen von Fr. Kohlrausch, II, Barth, Leipzig, 1911.
[21] KOHLRAUSCH and STEINWEHR, *Sitzber. preuss. Akad. Wiss.* (1902), p. 581.
[22] KOHLRAUSCH and MALTBY, *Sitzber. preuss. Akad.* (1899), p. 665.
[23] PARKER and PARKER, *J. Am. Chem. Soc.*, **46**, 312 (1924).
[24] WEILAND, *J. Am. Chem. Soc.*, **40**, 131 (1918).
[25] WALDEN and ULICH, *Z. physik. Chem.*, **106**, 49 (1923).
[26] KOHLRAUSCH, *Sitzber. preuss. Akad. Wiss.* (1900), p. 1002.
[27] SHERRILL, *J. Am. Chem. Soc.*, **32**, 741 (1910).
[28] JONES, *et al.*, *Carnegie Inst. Wash. Pub. No.* 180 (1913).
[29] KOHLRAUSCH and GROTRIAN, *Nachr. kgl. Ges. Wiss. Göttingen* (1874), p. 405.
[30] KOHLRAUSCH and GROTRIAN, *Ann. Physik Chem.*, **154**, 1 (1875).
[31] KOHLRAUSCH and GROTRIAN, *Ann. Physik Chem.*, **154**, 215 (1875).
[32] FOSTER, *Phys. Rev.*, **8**, 257 (1899).
[33] HARKINS and PAINE, *J. Am. Chem. Soc.*, **41**, 1155 (1919).
[34] WALDEN, *Z. physik. Chem.*, **1**, 529 (1887).
[35] FLÜGEL, *Z. physik. Chem.*, **79**, 577 (1912).
[36] KOHLRAUSCH, *Ann. Physik Chem.*, **6**, 145 (1879).
[37] KOHLRAUSCH, *Ann. Physik Chem.*, **26**, 161 (1885).
[38] CLAUSSEN, Dissertation, Rostock (1911).
[39] PFANHAUSER, *Z. Elektrochem.*, **7**, 698 (1901).
[40] MURATA, *Bull. Chem. Soc. Japan*, **3**, 47 (1928).
[41] LONG, *Ann. Physik Chem.*, **11**, 37 (1880).
[42] GOODWIN and HASKELL, *Phys. Rev.*, **19**, 369 (1904).
[43] LORENZ and OSSWALD, *Z. anorg. all gem. Chem.*, **114**, 209 (1920).
[44] NOYES and COOPER, *Carnegie Inst. Wash. Pub. No.* 63, 115 (1907).
[45] BROWNSON and CRAY, *J. Chem. Soc.* (London), **127**, 2923 (1925).
[46] LINDE, *Z. Elektrochem.*, **30**, 255 (1924).
[47] OSTWALD, "Lehrbuch der allgemeinen Chemie," Engelmann, Leipzig, 1891–1903.
[48] SMITH, *J. Am. Chem. Soc.*, **45**, 360 (1923).
[49] NOYES and EASTMAN, *Carnegie Inst. Wash. Pub. No.* 63, 239 (1907).
[50] VELEY and MANLEY, *Trans. Roy. Soc.* (London), A, **191**, 365 (1898).
[51] LINDNER, *Monatsh.*, **33**, 613 (1912).
[52] GIBSON and GIBSON, *Proc. Roy. Soc. Edinburgh*, **30**, 254 (1909).
[53] KOHLRAUSCH, *Ann. Physik Chem.*, **159**, 233 (1876).
[54] KOHLRAUSCH, *Ann. Physik Chem.*, **17**, 69 (1882).
[55] HEYDWEILLER, *Ann. Physik*, **48**, 681 (1915).
[56] BOUSFIELD and LOWRY, *Trans. Roy. Soc.* (London), A, **204**, 253 (1905).
[57] NOYES and KATO, *Carnegie Inst. Wash. Pub. No.* 63, 151 (1907).
[58] RAIKES, YORKE, and EWART, *J. Chem. Soc.* (London) (1926), p. 630.
[59] BRAY and HUNT, *J. Am. Chem. Soc.*, **33**, 781 (1911).
[60] LAMBLE and LEWIS, *J. Chem. Soc.* (London), **107**, 233 (1915).
[61] PARKER, *J. Am. Chem. Soc.*, **45**, 2017 (1923).

The concentration of solid AgCl not dissolved is so large in comparison with the dissolved AgCl that it may be considered as a constant

$$(AgCl_{solid}) = k_3$$

It follows, then, that the product of the concentration of the silver ions times the concentration of the chloride ions is a constant

$$(Ag^+)(Cl^-) = k_1k_2k_3 = K$$

which is designated as the solubility product of silver chloride. The addition of silver ions to the solution, say from a soluble silver salt, will increase the concentration of the silver ions and, for the equilibrium to be maintained, necessarily decrease the concentration of the chloride ions which will be removed by reacting with silver ions to form un-ionized silver chloride. Inasmuch as the solution is already saturated in respect to silver chloride, it follows that any increase in concentration of the silver chloride will cause precipitation of this material until equilibrium values are restored. In a similar manner, the addition of an ion common to two salts, introduced through the medium of a second salt such as a chloride not containing silver, will tend to upset the equilibrium and cause precipitation of silver chloride unless the solubility of the silver chloride under the new set of conditions is also changed.

It is obvious that in solutions containing two or more salts, the conductivity of the solution will be affected by the equilibria set up by the ions and their concentrations, their interreaction, their solubilities, and the formation of different undissociated salts. The conductivity will be a summation of the ionic conductivities and their concentrations as they exist in the solution at the equilibrium point.

Newer Theories of Dissociation. The Arrhenius theory was developed to account for and correlated three common properties of acids, bases, and salts:

1. The heat and practically instantaneous exchange of radicals as compared with the slow reactions of organic chemistry.

2. The increase in equivalent conductivity with dilution to a finite limit set by the mobilities of the ions.

3. Van't Hoff's observation that the osmotic properties of this class of substances always exceeded that predicted by his gas law

equation $PV = nRT$, which he had demonstrated was valid for nonelectrolytes in dilute solution.

Although in the period 1805 to 1860 Clausius and Grotthus had proposed that electrolytes must be dissociated to a minute extent at the moment of double decomposition in order to account for property 1 and the phenomenon of conduction, it remained for Arrhenius to correlate the experiments of Kohlrausch and van't Hoff and to propose a method for determining the degree of dissociation, whereby he could demonstrate that a very considerable dissociation prevailed in aqueous solutions of salts at ordinary concentrations. Arrhenius was severely criticized at first for his view that KCl was about 86 per cent dissociated in 0.1 M solution, instead of minutely as Clausius had suggested. The net results of recent research have shown that the behavior of the typical strong electrolytes in solvents of high dielectric constant is best explained upon the assumption of complete, or at least practically complete, ionization.

In the newer theories the electric charges upon the ions are assumed to set up electrostatic fields which do not allow the ions to behave independently as demanded by the gas laws. The effects of these interionic attractions were entirely neglected in the development of the classical theory, whereas according to the modern point of view, the anomaly of strong electrolytes is to be attributed entirely to these interionic attractions.

Ever since the idea was proposed by Van Laar,[9] by Sutherland,[10] and by Bjerrum[11] that the electric fields of the ions must be taken into account in the study of strong electrolytes, many attempts have been made to calculate the magnitude of these effects from purely theoretical considerations. Milner[12] was the first to succeed. No theoretical objection can be raised to his methods, but they became so complicated mathematically that he was restricted to univalent salts. Even in this simple case he was forced to employ graphical approximations.

Debye and Hückel[13] developed a theory which is more simple

    [9] VAN LAAR, J. J., *Z. anorg. Chem.*, **139**, 108 (1924).

    [10] SUTHERLAND, W., *Phil. Mag.* (6), **3**, 161 (1902); **7**, 1 (1906).

    [11] BJERRUM, N., *Proc. Seventh Intern. Congr. of Applied Chem.* (London), Sec. X (1909); *Z. physik. Chem.* **24**, 321 (1918).

    [12] MILNER, S. R., *Phil. Mag.* (6), **25**, 742 (1913).

    [13] DEBYE, P., and HÜCKEL, E., *Physik. Z.*, **24**, 185, 344 (1923); *ibid.*, **25**, 97 (1924); *Ergeb. exakt. Naturw.*, **3**, 199 (1925).

mathematically than Milner's. The fundamental idea underlying the calculations of all three workers is that, owing to electrical attractions, an ion of a given sign will on the average be surrounded by more ions of unlike sign than by ions of like sign. When such a solution is diluted to a very large volume, the ions become separated to such an extent that their mutual electrostatic attractions are no longer of significance. A uniform random distribution then prevails, or in other words, the gas laws are valid.[14] If we can calculate the excess electrical work which is involved in this isothermal dilution due to the rearrangement of the relative position of the ions, we can then calculate the extent of the deviation from the gas laws in terms of the activity coefficient of the ions, or the osmotic deviation of the solvent by any of the familiar thermodynamic methods.

[14] DEBYE, P., *Trans. Am. Electrochem. Soc.*, **51**, 499 (1927); LaMER, V. K., *ibid.*, **51**, 507 (1927); HARNED, II. S., *ibid.*, **51**, 571 (1927); DOLE, M., "Principles of Experimental and Theoretical Electrochemistry," McGraw-Hill Book Company, Inc., New York, 1935; MACINNES, D. A., "The Principles of Electrochemistry," Reinhold Publishing Corporation, New York, 1939; GLASSTONE, S., "Introduction to Electrochemistry," D. Van Nostrand Company, Inc., New York, 1942.

CHAPTER 4

ELECTROMOTIVE FORCE AND ENERGY RELATIONS

So far only the quantitative factor of electrical energy has been considered. In this chapter the intensity factor or difference of potential, often referred to as electromotive force (emf) or voltage, will be discussed. It is of particular interest to study the differences of potential produced by voltaic or galvanic cells, which may be defined as any arrangement by which the energy of chemical reactions or of certain physical processes, such as diffusion, is converted into electrical energy.

If a chemical reaction be written in its complete form or in the thermodynamic manner, energy changes resulting from the chemical reaction are written as a portion of the equation. Commonly the energy values are in thermal units and may be put on a gram-equivalent or gram-molar basis. For example,

$$2B + A \rightleftharpoons B_2A \pm Q \text{ cal}$$
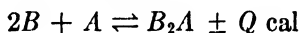
or in terms of equivalents,

$$B + \frac{A}{2} \rightleftharpoons \frac{B_2A}{2} \pm \frac{Q}{2} \text{ cal}$$

or $Q/2$ cal per gram equivalent of B, A, or B_2A.

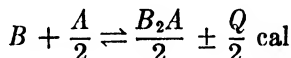For a particular constituent, the reaction may be set up to consume or produce 1 gram equivalent which, in an electrochemical manner at 100 per cent current efficiency, would be produced by a faraday, or 96,500 coulombs. The thermal unit includes both the quantity and potential factors, while the faraday is only the quantity factor and, when multiplied by the intensity factor or voltage, will be equal to the thermal energy.

If, therefore, the thermal energy per gram equivalent be converted into electrical energy in joules, then

$$1 \text{ cal} = 4.183 \text{ joules}, \qquad 1 \text{ joule} = 0.2387 \text{ g cal}$$

then

$$\frac{Q}{2} \text{ cal} \times 4.183 = 2.092Q \text{ joules per gram equivalent}$$

The electrical energy divided by the faraday in coulombs will result in a quotient of joules or watts per second divided by coulombs or amperes per second, both figures being in terms of a gram equivalent, as

$$\frac{2.092Q \text{ joules}}{F(96,500 \text{ coulombs})} = \frac{\text{watt-seconds}}{\text{ampere-seconds}} = \text{volts}$$

The quotient, in volts, will be an approximation for the theoretical decomposition potential of the reaction under the thermodynamic conditions for which it was written.

From the large collection of thermochemical data, heats of formation of compounds, heats of reaction, heats of dilution, as well as other thermal values, applications may be made of energy values to electrochemical systems and reactions. It is obvious that the quantity of heat necessary to balance a reaction thermally will not be entirely available as electrical energy. Some of the heat will be lost under the conditions of operation and not be entirely converted into electrical energy, while some of the electrical energy produced may be degraded into heat not only in the electrochemical cell but through resistances in the external circuit, contact drops, film resistances, as well as other factors. It can be seen that, in the application of electrical energy to reverse an exothermic reaction, the mechanism employed will necessarily be an imperfect one and the voltage applied to the circuit will be higher than the theoretical decomposition voltage. Conversely, if the chemical reactions be caused to produce electrical energy, the voltage calculated from the reaction will be the maximum possible.

Primary cells are electrochemical machines for the conversion of chemical energy into electrical work. The reactions in the Daniell cell (consisting of zinc in its metallic form immersed in an aqueous solution of $ZnSO_4$, which in turn is divided from an aqueous solution of $CuSO_4$ by a porous membrane, into which $CuSO_4$ solution a metallic copper electrode dips) produce some form of energy which can be completely controlled and directly utilized for any desired purpose. When the circuit in the Daniell cell or "battery" is completed by connecting the zinc and copper electrodes to a conductor, current flows from the copper to the zinc. Zinc metal passes into solution as zinc ion. From the chemical viewpoint, the zinc is oxidized in that its valence

changes from zero to a higher value. Copper, in solution as copper ion, is reduced to metallic copper and deposited on the copper electrode. Inasmuch as the cell produces electrical energy, this must result from the condensed reaction

$$Zn + Cu^{++} = Zn^{++} + Cu$$
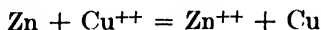
When a $CuSO_4$ solution and metallic zinc are brought together, the resulting chemical reaction is accompanied by the evolution of heat. If this reaction were carried out in a calorimeter starting and ending at the same temperature, and the heat liberated were measured, the total heat evolved would be equal to the decrease of total energy of the system. This value will be denoted by U. The difference between the heats of formation of $ZnSO_4$ and $CuSO_4$ solutions for the concentrations of $CuSO_4 \cdot 100H_2O$ and $ZnSO_4 \cdot 100H_2O$ is 50,110 cal per gram molecule at 0°C.

Chemical and Electrical Energy. If an external voltage be applied to the Daniell cell, the reaction can be reversed or made to go from right to left. It can be seen then, that when the reaction is proceeding from left to right, current will be needed in order to reverse the reaction.

Suppose the cell be operated isothermally or at constant temperature, until 1 gram equivalent of zinc has been converted from the metallic to the ionic state and 1 gram equivalent of copper reduced from the ionic to the metal state. Let E be the voltage produced by the cell and EF will be the energy liberated and converted into heat. Then an external voltage is applied to the cell with a voltage correction for the cell resistance, and current is fed to the cell until there is a complete reversal, the deposited copper being converted to ionic form and the ionic zinc converted to metallic form to the extent of 1 gram equivalent in each case. If the net voltage be E_1, resulting from the difference between the applied voltage and that small amount necessary to overcome the resistance of the cell, the energy fed to the cell will be E_1F, and E_1 will be greater than E. The cell has been restored to its original condition by a reversible process, and $(E_1 - E)F$ joules have been dissipated as heat.

A number of studies on primary cells have shown that the terminal voltage is a function of the current drawn from the cell. With infinitely small currents, the voltage will reach its maximum or open-circuit value. Conversely, the voltage will reach its

minimum when the current output is the largest possible. Side reactions, film resistances, generally grouped under the term "polarization," will affect the cell output. The greater the current forced into the cell, the higher the necessary voltage which must be applied across the terminals. With an infinitely small current, the minimum value of applied voltage approaches the emf of the cell as a limit.

The maximum amount of electrical energy can be obtained only from a cell working isothermally if the operation proceed reversibly. This follows from the second law of thermodynamics which states that in any isothermal process the maximum amount of external work is obtained when the process is conducted reversibly.

In a reversible process involving the conversion of energy, we may write

$$U = A - Q$$

where Q is the heat absorbed by the system[1] and A represents the external work done by the system when its total energy decreases by U. In the conversion of chemical to electrical energy, this electrical energy will have a maximum value equal to A. In electrical units $A = nFE$, where n is the number of equivalents involved. If it be assumed that Q is negligible, then

$$U = nFE$$

and

$$E = \frac{U}{nF}$$

which gives us a method of determining the emf of a cell from thermochemical data, or the theoretical decomposition voltage of a compound.

Gibbs-Helmholtz Equation. The relation between electrical energy of a system and the heat of reaction is given by the Gibbs-Helmholtz equation

$$A - U = T\frac{dA}{dT}$$

in which T is the absolute temperature. In a system in which a chemical reaction takes place, the amount of external work is

---

[1] Following the custom of thermodynamics, heat developed by a reaction is taken as negative.

small. A approaches zero as a limit, and we may write

$$U = -Q$$

By substitution in the Gibbs-Helmholtz equation for A and U, we obtain

$$nFE + Q = T \frac{nF dE}{dT}$$

whence

$$E = \frac{-Q}{nF} + T \frac{dE}{dT}$$

If E be expressed in volts and Q in calories, then

$$E = \frac{-JQ}{nF} + T \frac{dE}{dT}$$

where $J = 4.182$ is the electrical equivalent of heat. It will be observed that, when dE/dT is positive, the emf of a reversible voltaic cell increases with rise in temperature; when zero, the electrical energy is equal to the chemical energy.

The Gibbs-Helmholtz equation has been checked quantitatively by a number of workers.[2] From the results obtained it has been shown that heats of reaction may be determined by emf measurements. The equation also allows the determination of the theoretical voltage of a cell for the calculation of the theoretical energy and energy efficiency.

Electrolytic Solution Pressure. Analogous to vapor pressure of a liquid or solid, Nernst[3] assumed the existence of a definite tendency toward the passage from the atomic to the ionic state which he designated as electrolytic solution pressure p. In general, the values decrease in the same order as the increase of the electropositive character of the metal. The nonmetals are also assumed to have electrolytic solution pressures, the order in the case of the halogens and sulfur being fluorine, chlorine, bromine, iodine, and sulfur.[4]

---

[2] JAHN, H., *Wied. Ann.*, **50**, 189 (1893); BUGARSZKY, ST., *Z. anorg. Chem.*, **14**, 145 (1897); COHEN, E., CHATTAWAY, F. D., and TOMBROK, W., *Z. physik. Chem.*, **60**, 706 (1907).

[3] NERNST, W., *Z. physik. Chem.*, **4**, 150 (1889).

[4] In accordance with Nernst's assumption, if a bar of metal such as zinc be placed in water, each of the zinc atoms gives up two electrons to the bar of metal and passes into the water as positively charged zinc ion. An electric

Electrode Potentials. In the Daniell cell the zinc in $ZnSO_4$ is negatively charged with respect to the $CuSO_4$. The potential difference between the two solutions, $ZnSO_4$ and $CuSO_4$, in the cell is negligible. It follows, therefore, that the copper is at a positive potential in respect to zinc. The difference of potential between the electrode and the solution around it is termed the "single electrode potential." The emf of the cell is given by the potential difference between the copper and zinc strips with open external circuit. It is therefore equal to the difference of the single electrode potentials. Then

$$E = e_1 - e_2$$

where e_1 and e_2 are single electrode potentials. If various cells be set up and their emf measured, it is readily possible to determine the difference between the values of any two single electrode potentials. For a determination of their absolute values, however, a completely satisfactory method is not available. The absolute values would be important in that they would indicate at once whether a process occurring at a given electrode involve an increase or decrease of free energy. For convenience, the

double layer is thus formed at the junction of the metal and the liquid. Opposing the passage of the atoms to the ionic state is the electrostatic attraction of the negative charges which accumulate at the metal surface. The establishment of equilibrium is so rapid that the amount of zinc appearing in the form of ions cannot be detected analytically. In the case of copper, the number of negative charges necessary to prevent the passage of atoms of this metal into the ionic state is very much smaller than in the case of zinc, in that the electrolytic solution pressure of copper is infinitesimal. If a piece of zinc be immersed in a solution of $CuSO_4$, copper ions will discharge and deposit as copper atoms on the zinc. The negative charges on the zinc will be reduced and more zinc atoms will be able to assume the ionic state. The amount of zinc entering solution will be equivalent to the amount of copper deposited. When any metal is immersed in a solution of a salt of another metal having a lower electrolytic solution pressure, the latter metal is deposited, and the former enters solution. The concept of electrolytic solution pressure enables us to understand why some metals are displaced by others from solution, and why certain metals are dissolved by acids and others are not. When a piece of metal having a high electrolytic solution pressure is immersed in a solution containing its own ions, the tendency of the atoms to pass into the ionic state is opposed by the osmotic pressure P of the metal ions in solution. The relative values of the osmotic pressure and the electrolytic solution pressure will determine whether ions leave or enter solution.

normal hydrogen electrode is chosen as the standard and a single potential of zero assigned to it.   The normal hydrogen electrode proposed by Nernst consists of a piece of well-platinized platinum attached to a conductor and immersed in a H_2SO_4 solution containing 1 gram equivalent of hydrogen ion.   Pure hydrogen is bubbled around this electrode and adsorbed or dissolved in the platinum to form an electrode which is reproducible.   The emf of this electrode against the normal calomel (*i.e.*, HgCl Hg) at 25°C is -0.2822, and the absolute emf is then $+0.2826$. When the emf of cells is produced by combining hydrogen electrodes with other electrodes, the values obtained are termed "single electrode potentials," in that an arbitrary value of zero is assigned to hydrogen.   The absolute potentials are therefore the potentials against the hydrogen electrode plus 0.2826. Gerke[5] gives the potential E of an electrochemical reaction as following the equation

$$E = E_0 - \frac{0.05915}{N} \log_{10} \frac{(A_P)^x}{(A_R)^y}$$

where N is the number of faradays in the equation of the reaction, A_P and A_R the activities of the reactants, and x and y the corresponding coefficients in the electrochemical equation.   .

In order to indicate the direction of the polarity between a metal and a solution, the sign of the charge on the metal is placed before the potential difference between the two phases—the so-called "potential of the metal" or the "electrode potential."[6] In solutions containing their own ions, noble metals (*e.g.*, with electrolytic solution pressures lower than that of hydrogen) acquire a positive potential, whereas base metals (*e.g.*, with electrolytic solution pressures greater than that of hydrogen) acquire a negative potential.   In accordance with this convention

---

[5] GERKE, R. H., "International Critical Tables," Vol. VI, p. 332, McGraw-Hill Book Company, Inc., New York.

[6] W. D. Bancroft [*Trans. Am. Electrochem. Soc.*, **33**, 79 (1918)] maintains this convention is the only one of universal application.   It is the official standard of the Bunsen Gesellschaft, The Electrochemical Society, the National Bureau of Standards of the U.S., and has been accepted by most continental electrochemists.   G. N. Lewis [*J. Am. Chem. Soc.*, **35**, 1 (1913)] suggested a convention of considering the potential difference of a metal-solution junction as positive when current tends to flow from left to right and negative as the reverse, considering the junction as written.

the potential of a metal in contact with a solution containing its own ions is positive when p is less than P and negative when p is greater than P.

A short arrow will sometimes be placed above a metal-solution junction to indicate the direction in which the positive current tends to flow. When the arrow points toward the metal, its potential is positive; when it points away from it, its potential is negative.

According to Nernst's theory, the magnitude of a single electrode potential will be a function of the electrolytic solution pressure of the metal and of the osmotic pressure of the metal ions in the solution. For equilibrium reactions involving anodic oxidation of the type of a metal passing into solution and forming ions by the loss of electrons, or the reverse reaction at the cathode —*i.e.*, the deposition of the metal and the gain of the electrons (valence increases represent loss of electrons, and valence decreases gain of these)—Nernst deduced the relation

$$neF = -RT \ln \frac{p}{P}$$

on the assumption that the gas laws are valid for ions of strong electrolytes.[7] For dilute solutions osmotic pressure varies with concentration. Then $P = kc$, where c in gram ions per liter is the concentration of metal ions and k is a constant. Then

$$neF = -RT \ln \frac{p}{kc}$$
$$e = -\frac{RT}{nF} \ln \frac{p}{k} + \frac{RT}{nF} \ln c$$

For a given pure metal the term $- (RT/nF) \ln (p/k)$ is a constant at a given temperature and may be written e_0 or the normal electrode potential of the equilibrium in question. At 25° $T = 298$, $R = 8.32$ joules, and after converting natural to Briggs logarithms the electrode potential for the cation is

$$e = e_0 + \frac{0.059}{n} \log c$$

---

[7] Where p is the electrolytic solution pressure of metal M, P the osmotic pressure of the metal ions in solution, e the single electrode potential corresponding to the equilibrium, R the gas constant, and T the absolute temperature.

and for the anion

$$e = e_0 - \frac{0.059}{n} \log c$$

In a normal solution c is unity, $e = e_0$. We then have a definition of electrode potential as the potential difference between the electrode material and a normal solution (one gram ion per liter) of the ion in the equilibrium.

A table of electrode potentials will furnish data as to the quantitative aspect of electrode equilibriums in a concise form. Table 4 gives the more important single potentials. The values have been taken from Gerke, "International Critical Tables" Vol. VI, McGraw-Hill Book Company, Inc., by permission. The order of the elements is that of the well-known electromotive series of the metals.

Gas Electrodes. In addition to electrode reactions between metal electrodes and metal ions, we may have gas electrodes in that hydrogen, the halogens, and oxygen also are known to ionize. Nitrogen, however, does not ionize. To render these gases electromotively active, they are best bubbled through an electrolyte containing the ion concerned, in which solution there is a piece of platinized platinum half immersed. The gases are soluble or adsorbed in the platinum and can then ionize. The electrolytic solution pressure of a gas dissolved in platinum varies directly with the amount of gas in the metal, which in turn varies directly with the gas pressure in the surrounding space.

Oxidation and Reduction Cells. According to the classical definition, the process of oxidation involves the loss of electrons from the atom or ion, while the reduction process involves the gain of electrons. At an anode the passage of a metal from its elemental form with an apparent zero valence to its ionic form under the action of the electric current involves a loss of electrons and a gain in valence:

$$M - \ominus \rightarrow M^+$$
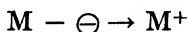
Oxidation reactions are therefore associated with the anode. Conversely, at the cathode the positive ions are discharged and are converted to their elemental form with a gain of electrons and a decrease in valence:
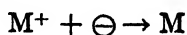
$$M^+ + \ominus \rightarrow M$$

TABLE 4. ELECTRODE POTENTIALS

Reaction	Volts	Reference	Equation	Volts	Reference
$Li^+ + e = Li$	−2.959	(1)			
$Rb^+ + e = Rb$	−2.925	(1)			
$K^+ + e = K$	−2.924	(1)			
$Ca^{++} + 2e = Ca$	−2.76	(2)			
$Na^+ + e = Na$	−2.714	(1)			
			$Ba^{++} + 2e = BaHg$	−1.570	(6)
			$NaCl + e = NaHg + (Cl^-$ in sat. NaCl)	−1.837	(7)
			$Sr^{++} + 2e = SrHg$	−1.793	(6)
$Zn^{++} + 2e = Zn$	−0.761	(1)			
$Cr^{++} + 2e = Cr$	−0.557	(3)			
$Fe^{++} + 2e = Fe$	−0.44	(1)			
$Cd^{++} + 2e = Cd$	−0.401	(1)			
			$Tl^+ + e = TlHg$	−0.336	(1)
$Ni^{++} + 2e = Ni$	−0.23	(4)			
$Sn^{++} + 2e = Sn$	−0.136	(1)			
$Pb^{++} + 2e = Pb$	−0.122	(1)			
$H^+ + e = \frac{1}{2}H_2$	0.000				
			$Sb_2O_3 + 6H + 6e = 2Sb + 3H_2O$	0.144	(8)
			$BiOCl + 2H^+ + 3e = Bi + Cl^- + H_2O$	0.158	(9, 10)
			$As_2O_3 + 6H^+ + 6e = 2As + 3H_2O$	0.234	(11)
$Cu^{++} + 2e = Cu$	0.344	(1)			
$Ag^+ + e = Ag$	0.797	(1)			
$Hg_2^{++} + 2e = 2Hg$	0.798	(1)			
$Au^{+++} + 3e = Au$	1.36	(5)			

[1] LEWIS and RANDALL, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc., New York, 1923.
[2] DRUCKER and LUFT, *Z. physik. Chem.*, **121**, 307 (1926).
[3] GRUBE and BREITINGER, *Z. Elektrochem.*, **33**, 112 (1927).
[4] HARING and VANDEN BOSCHE, *J. Phys. Chem.*, **33**, 161 (1929).
[5] JIRSA and JELLINEK, *Chem. Listy*, **18**, 1 (1924); *Z. Elektrochem.*, **30**, 286 (1924).
[6] DANNER, *J. Am. Chem. Soc.*, **46**, 2385 (1924).
[7] DANNER, *J. Am. Chem. Soc.*, **44**, 2832 (1922).
[8] SCHUHMANN, *J. Am. Chem. Soc.*, **46**, 52 (1924).
[9] JELLINEK and KÜHN, *Z. physik. Chem.*, **105**, 337 (1923).
[10] NOYES and CHOW, *J. Am. Chem. Soc.*, **40**, 739 (1918).
[11] SCHUHMANN, *J. Am. Chem. Soc.*, **46**, 1444 (1924).

At the anode, negative ions are discharged with a loss of electrons and a gain in valence:

$$A^- - \ominus \rightarrow A$$
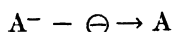
They are therefore oxidized. It is obvious that the oxidation-reduction reactions as stated here involve the concept of negative and positive valences. It is to be noted that the reduction reactions at the cathode may take place in a stepwise fashion, an

example of which is the reduction of ferric to ferrous ions

$$Fe^{+++} + \ominus \rightarrow Fe^{++}$$
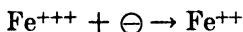
and a converse reaction may take place at the anode.

In the discussion above, the oxidation-reduction reactions occurred through the medium of the electric current. Contrariwise, an electric current may readily be produced by a suitable arrangement of the constituent parts of these reactions. The cells set up must be such that simultaneous loss and gain of electrons occur but in separate localities, with connections made in such a way that the transfer of electrons or the flow of electricity is possible. Such cells are called "oxidation-reduction cells." A typical example would be a platinum electrode dipping into a solution of ferric sulfate, connected by a salt bridge to a solution of copper sulfate into which a copper electrode dipped, and a wire connection made between the platinum and the copper. The flow of current externally would be from the platinum to the copper, and in the cell the copper would be oxidized to copper ions and the ferric ion reduced at the cathode to the ferrous state. Similarly, a platinum electrode dipping into a solution of stannous salts joined to form a cell with a platinum electrode dipping into stannic solution would be of the oxidation-reduction type.

The tendency of the ion to pass from one valence to another could be determined by emf measurements, and the value derived is the oxidation potential. It follows, therefore, that an ion of higher oxidation potential will oxidize one which shows a lower value. The ion of relatively lower oxidation potential is the reducing agent under the particular set of conditions. Thus the same ion may serve as a reducing agent for one substance and an oxidant for others.

For a reaction of the type

$$M^x \rightleftharpoons M^y + (x - y)\ominus$$

the potential difference varies with ionic concentration according to the equation

$$e = e_0 + \frac{RT}{nF} \ln \frac{c}{c'}$$

TABLE 5. REDUCTION REACTIONS

Reaction	Volts	Ref.
$Cr^{+++} + e = Cr^{++}$	-0.40	(1, 2)
$Cu_2O + H_2O + 2e = 2Cu + 2OH^-$	-0.34	(3)
$CuS + 2H^+ + e = Cu + H_2S$	-0.259	(4)
$SbO + 2H^+ + 3e = Sb + H_2O$	-0.212	(5)
$PbS + 2H^+ + 2e = Pb + H_2S$	0.07	(4)
$PbO_2 + H_2O + e = PbO + 2OH^-$	0.27	(6)
$Ti^{+++} + e = Ti^{++}$	0.37	(7)
$Cu^{++} + 2Cl^- + e = CuCl_2^-$	0.455	(8)
$K_3Fe(CN)_6 + K^+ + e = K_4Fe(CN)_6$	0.486	(9)
$H_3AsO_4 + 2H^+ + 2e = H_3AsO_3 + H_2O$	0.57	(10)
$MnO_4^- + e = MnO_4^{--}$	0.664	(11)
$Fe^{+++} + e = Fe^{++}$	0.747	(12, 13)
$Tl^{+++} + 2e = Tl^+$	1.21	(14)
$Sn^{++++} + 2e = Sn^{++}$	1.25	(15)
$MnO_2 + 4H^+ + 2e = Mn^{++} + 2H_2O$	1.33	(16)
$Ce^{++++} + e = Ce^{+++}$	1.55	(17)
$MnO_4^- + 4H^+ + 3e = MnO_2 + 2H_2O$	1.58	(18)
$Co^{+++} + e = Co^{++}$	1.81	(19, 20)

[1] FORBES and RICHTER, *J. Am. Chem. Soc.*, **39**, 1140 (1917).
[2] GRUBE and BREITINGER, *Z. Elektrochem.*, **33**, 112 (1927).
[3] ALLMAND, *J. Chem. Soc.* (London), **95**, 2151 (1909).
[4] KNOX, *Trans. Faraday Soc.*, **4**, 29 (1908).
[5] SCHUHMANN, *J. Am. Chem. Soc.*, **46**, 52 (1924).
[6] GLASSTONE, *J. Chem. Soc.* (London), **121**, 1456 (1922).
[7] FORBES and HALL, *J. Am. Chem. Soc.*, **46**, 385 (1924).
[8] CARTER and LEA, *J. Chem. Soc.* (London), **127**, 499 (1925).
[9] LEWIS and SARGENT, *J. Am. Chem. Soc.*, **31**, 355 (1909).
[10] FOERSTER and PRESSPRICH, *Z. Elektrochem.*, **33**, 176 (1927).
[11] SACKUR and TAEGENER, *Z. Elektrochem.*, **18**, 718 (1912).
[12] NOYES and BRANN, *J. Am. Chem. Soc.*, **34**, 1016 (1912).
[13] POPOFF and KUNZ, *J. Am. Chem. Soc.*, **51**, 382 (1929).
[14] GRUBE and HERMANN, *Z. Elektrochem.*, **26**, 291 (1920).
[15] FORBES and BARTLETT, *J. Am. Chem. Soc.*, **36**, 2030 (1914).
[16] TOWER, *Z. physik. Chem.*, **32**, 566 (1900).
[17] BAUR and GLAESSNER, *Z. Elektrochem.*, **9**, 534 (1903).
[18] BROWN and TEFFT, *J. Am. Chem. Soc.*, **48**, 1128 (1926).
[19] JAHN, *Z. anorg. allgem. Chem.*, **60**, 292 (1908).
[20] LAMB and LARSON, *J. Am. Chem. Soc.*, **42**, 2024 (1920).

where e is the emf produced by the reduction of M^x to M^y, c is the concentration of M^x, c' is the concentration of M^y, e_0 is the emf of the cell when $c/c' = 1$, n is the difference in the valence, R the gas constant, T the absolute temperature, and F the value of the faraday.

Table 5 gives representative values of oxidation-reduction potentials for some common systems.

Concentration Cells. In these we may have potential differences between two identical electrodes, one surrounded by a higher concentration of the same electrolyte than is the other. If any liquid potential difference be neglected from the general equation for the emf of an element, $E = e - e'$, which becomes, when both electrodes give cations,

$$E = e_0 - e_0' + \frac{0.058}{n} \log c - \frac{0.058}{n'} \log c'$$

Since the electrodes and the ions are the same,

$$E = \frac{0.058}{n} \log \frac{c}{c'}$$

The emf of a concentration cell is a function of the ratio of the ionic concentrations at the two electrodes. These emfs seldom reach large values save when the concentration ratio is very great.

In many cases the emf of a concentration cell at ordinary temperatures, after correction for liquid junction potential, shows a deviation from the value calculated from the formula where the values of ionic concentration are obtained from conductivity data. Strictly, the activity[3] a and a' of the ions should be substituted. At extreme dilution the values are identical, but they differ to some extent at moderate concentrations.

Measurement of Electrode Potentials. Single electrode potentials may be measured by combining the electrode whose value is desired with a standard electrode. The latter may be either the standard hydrogen electrode or some other, the potential of which is accurately known on the hydrogen scale. The emf of the galvanic cell thus formed is then measured potentiometrically. The unknown single potential can be calculated from the equation wherein the voltage of the cell equals the difference of the single potentials of the electrodes forming the cell.

The standard electrodes most commonly used are the normal and tenth normal calomel electrodes in which the system is $Hg | KCl$ solution saturated with $HgCl$. Such a so-called half cell is shown in Fig. 5. The potential of the normal calomel electrode $Hg | HgCl$ N KCl is $+0.286$ volt at 18°C and that of

[3] LEWIS, G. N., and RANDALL, M., "Thermodynamics," McGraw-Hill Book Company, Inc., New York, 1923.

the decinormal, Hg|HgCl 0.1N KCl, is $+0.338$ volt at 18°C. For use with alkaline solutions the cells Hg|HgO N NaOH($e = +0.117$ volt at 18°) and Hg|HgO 0.1N NaOH ($e = +0.72$ volt at 18°) are most useful.

For use with acid solutions, the standard hydrogen electrode ($e = \pm 0.0$ volt) is satisfactory, but the systems Hg|Hg$_2$SO$_4$ N H$_2$SO$_4$ ($e = +0.685$ volt at 18°) and Hg|Hg$_2$SO$_4$ 0.1N H$_2$SO$_4$ ($e = +0.687$ volt at 18°) are more convenient.

Connection between the electrode being measured and the standard electrode is made by a bridge of a high conductivity electrolyte such as KCl in the case of the normal calomel electrode.

It is sometimes desirable to measure the potential difference at an electrode during the course of electrolysis.[9] In this case the siphon side tube of the half cell is very much lengthened, bent horizontally at the end, and drawn to a fine point which can be brought up immediately against the electrode being studied. The error introduced as the result of the potential drop caused by the current is very low, seldom exceeding 0.002 volt.

KCl saturated with Hg$_2$Cl$_2$

Hg$_2$Cl$_2$

Hg
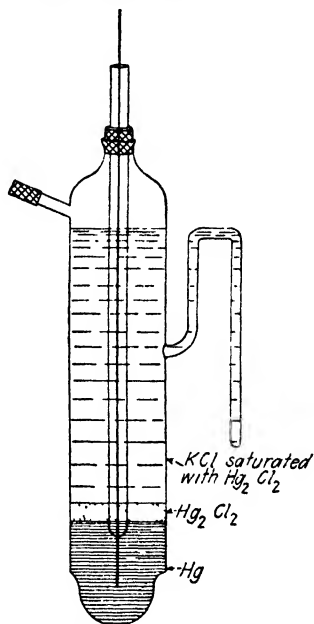
Fig. 5.   Half cell.

Energy Efficiency. Conditions are never reached in practice where an electrolysis may be conducted in a truly reversible manner without side reactions, or without ohmic-resistance effects of the electrodes, and the electrolyte, and at every contact or junction between the electrodes and their connectors or electrodes and the electrolyte. The theoretical quantity of electrical energy needed for the production of one equivalent would be the value of the faraday times the theoretical decomposition voltage for the reaction. The units are volt-coulombs or watt-seconds.

It has been noted that it is decidedly unusual to reach 100 per cent current efficiency due to side reactions or thermal effects.

[9] HARING, H. E., *Trans. Am. Electrochem. Soc.*, **49**, 417 (1926).

For reasons stated above, electrolysis very seldom proceeds at theoretical decomposition voltages. The ratio between the theoretical energy and the actual is the energy efficiency expressed as a percentage. The amount of energy used in practice is always larger than the theoretical. If the theoretical be divided by the actual voltage to give a value of voltage efficiency, then energy efficiency may be described as the product of the current and voltage efficiencies.

Measurement of Decomposition Voltages. It is often necessary to measure decomposition voltages experimentally when the values of the two single potentials of the electrodes are not known. An external emf is applied to the cell through a variable resistance with a voltmeter and an ammeter in the circuit. At the beginning the variable resistance is made very large. It is gradually decreased and simultaneous readings of the voltage and current are taken. Sudden increase in current occurs at the decomposition voltage point. For different reactions the curves may have different slopes and somewhat different shapes, as indicated in Fig. 6. For strictly accurate results, carefully calibrated meters should be employed and corrections for the small currents and the cell resistance made.
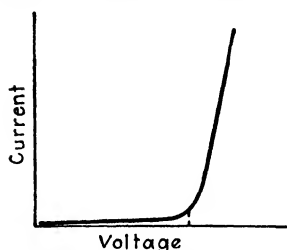
Fig. 6. Decomposition voltage curve.

If the cell be operated for some time and deposition products collect on the electrodes, the cell may then be short-circuited through a well-damped high-resistance voltmeter, whose reading will be the decomposition voltage of the electrolyte. This value is also termed the "back emf" of the cell.

The extent of polarization at any given current density is indicated on the decomposition voltage curve if the measurements be carried far enough. Measurement of single electrode potentials may be made during the passage of a current in any electrolytic cell. In general the potential of the electrode will change noticeably with increase of current through the cell. With an anode the potential becomes more positive, and with a cathode more negative as the current density is increased. If these relations be plotted, the c.d.-electrode potential curves are obtained. Different slopes of the c.d.-electrode potential curves

indicate different degrees of polarization as a function of the varying electrode processes.

LeBlanc[10] measured decomposition voltage of acids and bases as well as salts. He found that, for most acids and bases studied, the values were identical, and he concluded that the results measured the voltage necessary to decompose water. For salt solutions the results varied widely. Some of the values are given in Table 6.

TABLE 6. DECOMPOSITION VOLTAGES[1]

Electrolyte	Decomposition Voltage
Acetic acid.	1 57
Azoic acid.. ..	1 29
Dichloracetic acid..	1 66
Hydriodic acid..	0 52
Hydrobromic acid .	0 94
Hydrochloric acid...	1 31
Monochloracetic acid.	1 72
Nitric acid... .	1 69
Oxalic acid...	0 95
Perchloric acid ..	1 65
Phosphoric acid... ..	1 70
Sulfuric acid .	1.67
Trichloracetic acid . . .	1 51
Ammonium hydroxide.	1.74
Potassium hydroxide...	1 67
Sodium hydroxide . .	1.69
Cadmium nitrate..	1.98
Cadmium sulfate. .	2 03
Cobalt chloride	1 78
Cobalt sulfate ...	1 92
Copper sulfate....	1 49
Lead nitrate... .	1 52
Nickel chloride... .	1 85
Nickel sulfate....	2 09
Silver nitrate..	0 70
Silver sulfate...	0.80
Zinc bromide.	1 80
Zinc sulfate....	2.55

[1] LeBLANC, M., *Z. physik. Chem.*, **8**, 299 (1891).

[10] LeBLANC, M., *Z. physik. Chem.*, **8**, 299 (1891); "A Text-book of Electrochemistry," Chap. VIII, The Macmillan Company, New York, 1907.

MOLTEN ELECTROLYTES[2]

Electrolyte	Temperature, °C	Decomposition voltage
Potassium hydroxide...	200	2 4
Potassium hydroxide.....	300	2.35
Sodium hydroxide....	200	2.32
Sodium hydroxide...... . .	300	2 25
Sodium hydroxide...... . .	480	1.95[3]
Barium chloride........	650	3 05
Calcium chloride.	585	2 85
Lithium chloride.......... . ..	630	2.62
Potassium chloride.......... ..	810	2.8
Sodium chloride.......	835	2.6
Strontium chloride........	615	3.0

[2] NEUMANN and BERGVE, *Z. Elektrochem.*, **21**, 143 (1915).
[3] FLECK and WALLACE, *Trans. Faraday Soc.*, **16**, 346 (1921).

CHAPTER 5

ELECTROLYSIS AND POLARIZATION

It has been shown that the Nernst equation for emf applies to electrolytic cells for small currents. When, however, an appreciable current is passing across the boundary between an electrode and a solution, the value of the potential difference between the two is changed from its equilibrium value as given by the Nernst equation. The difference between these two values is called "polarization." Complete or partial removal of this difference is termed "depolarization." Any agent which does this work is called a "depolarizer."

Electromotive forces of galvanic cells measured by null methods with no current flowing are reversible; with currents of appreciable magnitude the potentials associated with this polarization are irreversible. LeBlanc[1] showed that polarization potentials and potential differences in voltaic cells are related in character. Lewis and Jackson[2] attributed polarization to reverse emfs caused by the depletion of the substances used in the electrolysis at a rate faster than they can be supplied, or by the accumulation of the products at a rate greater than their removal.

The increase in value of the potential of an electrode over the normal reversible potential is called "overvoltage." The decomposition voltage of an electrolyte varies with the nature of the electrodes, their surface conditions, previous history, and homogeneity, between which the solution is electrolyzed. The difference between the electrode potential necessary for the flow of current and the equilibrium value of the electrode with no current flowing is called the "overvoltage of the electrode." It can be seen that there are thus overvoltages for the various products of electrolysis, for the various electrodes at which they are liberated.

[1] LeBlanc, M., Z. physik. Chem., **8**, 299 (1891); **12, 333** (1893).

[2] Lewis, G. N., and Jackson, R. F., Proc. Am. Acad. Arts Sci., **41**, 399 (1906).

Electrode processes occur at the interfaces of the electrodes and the electrolyte, or in thin films adjacent to these electrodes. The bulk of the electrolyte may be considered merely as a reservoir for ions and as a conducting medium. At the cathode the discharge of an ion would tend to reduce the concentration of the ions in the cathode film. As a result, the single potential of the electrode tends to become more negative and cathodic polarization begins. With higher current density the concentration of the ions in the cathode film will tend to be lessened. Diffusion of ions from the body of the electrolyte to the area around the cathode will to some extent counterbalance this process. It is readily apparent that mechanical agitation, movement of the electrolyte, and similar processes will reduce the concentration polarization. A similar set of conditions holds true for the anode, with the exception that the single potential of the anode becomes more positive.

If the current become so large that the concentration of metal ions on the cathode surface is reduced practically to zero, no larger current can pass, however great the potential difference be made, unless some other ions begin to deposit. This value is termed the "limiting" or "maximum current." It depends upon the concentration, temperature, and rate of stirring of the solution.

Reversibility of Electrode Processes. Concentration polarization should not truly be considered as a form of polarization, inasmuch as the operation is reversible. If the electrodes be removed and similar reversible electrodes substituted for them, the emf measured would be the same.

Chemical reactions may take place which affect concentration polarization. In NaCl electrolysis with insoluble electrodes such as platinum, H^+ ion is deposited at the cathode, the supply being maintained by the dissociation of water into H^+ and OH^- ions. This reaction takes place when the removal of H^+ ions and the formation of hydrogen molecules disturb the water-ionization equilibrium. In some other cases chemical solution of the anode may occur in addition to the electrolytic reactions shown by the passage of the atoms of the anode into the ionic state. If the anode be an alloy, nonhomogeneous in nature or of such a character that one constituent is dissolved at a greater rate than another, there will then be an actual change in the

anode composition, with corresponding changes in the potential of the electrode. The potential may rise to a point where other electrode processes occur. If, for example, at the cathode a material different from the cathode is produced but showing solubility in the cathode material, say such as hydrogen with platinum, polarization takes place in that the platinum electrode is converted to a hydrogen electrode.

The phenomenon of passivity noted with many base metals as anodes in an electrolytic cell is related to, or is a form of, polarization. One theory proposes that the passivity is due to oxide films which are adsorbed on the surface of the metal. These films are more noble than the metal and interfere with the passage of the atoms to the ionic state. Chemical reactions and adsorption processes may interfere with the electrolysis. Insoluble films, nonconductive in their nature, may form on electrode surfaces, *e.g.*, $PbSO_4$ on lead anodes and $AgCl$ on silver anodes. Catalytic substances as constituents of electrodes may markedly affect polarization, in that they will accelerate one reaction and retard another, *e.g.*, the insoluble copper-silicon anode for copper electrolysis, whose catalytic surface accelerated the oxygen-evolution reaction and retarded the copper-solution process. In cases where insoluble films form on electrodes, they may so completely cover the surface that the ohmic resistance of the film is very high, and apparent large polarization values result. The ions of the electrolyte do not make contact with the electrode. Commercial utilization of this type of effect is found in anodic oxidation of aluminum and its alloys, tantalum, and other metals in rectifiers, electrolytic lightning arresters, etc.

Depolarization. In commercial practice, polarizations of all sorts may be considered as ohmic resistances forming part of the circuit. They are avoided as far as possible, for, if the polarization become too great, new electrode processes of an undesired nature may set in. It so happens, however, that in some cases polarization is definitely necessary for the production of the desired electrode process. This is true in the case of chromium deposition, where the hydrogen film on the cathode is the important factor in the production of the deposit of chromium metal. Polarization effects may markedly affect the types of deposits obtained. When they cannot be avoided by adjustment of current and voltage conditions, depolarizers are employed to

get rid of the undesired products.   An example of this is found in high-quality nickel plating where hydrogen in the nickel affects the ductility of the deposit.   Oxidizing substances like H_2O_2 are added to get rid of hydrogen codeposited with the nickel. In other electrode processes, additions of certain materials which will readily attack anodes are sometimes made to overcome anode polarization.   An example of this is the use of chlorides in various plating baths and in certain refining solutions to increase the rate of anode corrosion.

Overvoltage.   Two general methods exist for the measurement of overvoltage.   In one of these the electrode potential is determined while the current is flowing.   The tip of a bent tube of a standard electrode is placed against the electrode in question while the electrode is in the electrolytic cell.   Every attempt is made to minimize ohmic resistance.   In the other method the current applied to the electrolytic cell is shut off momentarily while the electrode potential is determined.   The first or the direct method was employed by Knobel and his associates;[3] the second was favored by Newbery.[4]   For hydrogen overvoltage, Newbery's work indicated that the value was related to the position of the metals in the periodic table, assigning nominal values for Group I of 0.35 volt, Group II 0.7 volt, Group III 0.5 volt, Group IV 0.45 volt, Group V 0.42 volt, Group VI 0.32 volt, Group VII 0.25 volt, and Group VIII 0.18 volt.

Values for hydrogen overvoltage for a number of materials in $2N$ H_2SO_4 as an electrolyte are given in Table 7 which is condensed from Knobel's data in the "International Critical Tables," McGraw-Hill Book Company, Inc., by permission.   The values vary directly with the current density, the extent of this increase usually being greater than accountable by concentration changes in the electrolyte.   Hydrogen overvoltages at very high current density for nearly all substances approach limiting values of about 1.3 volts.

From the figures given in the table, it will be seen that hydrogen overvoltage for most cathode materials is large enough to be of

[3] GOODWIN, H. M., and KNOBEL, M., *Trans. Am. Electrochem. Soc.*, **37**, 617 (1920); GOODWIN, H. M., and WILSON, L. A., *ibid.*, **40**, 173 (1921); KNOBEL, M., CAPLAN, P., and EISEMAN, M., *ibid.*, **43**, 51 (1923).

[4] NEWBERY, E., *J. Chem. Soc.*, **105**, 2420 (1914); **109**, 1051, 1066 (1916); *Mem. Proc. Manchester Lit. & Phil. Soc.*, **61**, No. 9 (1916).

practical importance even at moderate current density. The soft metals of low melting point show the highest hydrogen overvoltages, while those of high melting point have relatively small values.

TABLE 7. OVERVOLTAGE—$H_2{}^{1-6}$ AT 25°C
(Electrolyte 2N H_2SO_4)

Metal	Amperes per square centimeter				
	0.001	0.01	0.1	0.5	1.0
Aluminum.......	0.56	0.83	1.0	1.24	1.29
Bismuth.........	0.78	1.05	1.14	1.21	1.23
Brass....... .	0 50	0.65	0.91	1.23	1.25
Cadmium..	0.98	1.13	1.22	1.25	1.25
Carbon . . .	....	0.70	0.9	1.1	1.17
Copper	0.48	0.58	0.8	1.19	1.25
Duriron.. . .	0.20	0.29	0 61	0.86	1.02
Gold	0.24	0 39	0.59	0.77	0.80
Graphite. . .	0.60	0.78	0.98	1.17	1 22
Iron......	0.40	0.56	0.82	1.26	1 29
Lead	0.52	1.09	1.18	1.24	1.26
Mercury	0.9	1.04	1.07	1.1	1.12
Monel.	0.28	0.38	0.62	0.86	1.07
Nickel	0.56	0.75	1.05	1.21	1.24
Palladium	0 12	0.3	0.7	1.	1.
Platinum, platinized..	0.015	0.03	0.04	0.05	0.05
Platinum, smooth....	0.024	0.07	0.29	0.57	0.68
Silver..................	0.47	0.76	0.88	1.03	1.09
Tellurium........	0.4	0.45	0.48	0.54	0.6
Tin.............	0.86	1.08	1.22	1.24	1.23
Zinc....................	0.72	0.75	1.06	1.20	1.23

[1] KNOBEL, *J. Am. Chem. Soc.*, **46**, 2613 (1924).
[2] KNOBEL, *J. Am. Chem. Soc.*, **46**, 2751 (1924).
[3] KNOBEL, CAPLAN, and EISEMAN, *Trans. Am. Electrochem. Soc.*, **43**, 55 (1923).
[4] KNOBEL and JOY, *Trans. Am. Electrochem. Soc.*, **44**, 443 (1923).
[5] NEWBERY, *J. Chem. Soc.* (London), **105**, 2419 (1914).
[6] NEWBERY, *Trans. Faraday Soc.*, Part I, **15**, 126 (1919).

Many investigators have given attention to overvoltage. They have considered the condition of the electrode surface in that with rough surfaces the overvoltage is commonly lower; the purity of the metal of the electrode; the time of electrolysis in that with some materials maximum overvoltage is reached only after an appreciable time; temperature; the presence of colloids;

external pressures on the system; the effect of superimposed currents of varying frequencies in that alternating current lowers the overvoltage; surface tension; the effect of ultraviolet light; pH; adsorption phenomena, and minute amounts of impurities in the electrolyte or at the electrode-electrolyte interface.

Little attention has been paid to the effect of concentration of the electrolyte on the hydrogen overvoltage. In general the presence of colloids increases the overvoltage. The use of so-called "addition agents" in metal refining and the effect on the overvoltage will be discussed in some detail later. The reduction of external pressure seems to increase the hydrogen overvoltage slightly, while the superimposition of an alternating current on a direct current lowers the value.[5]

TABLE 8.   OVERVOLTAGE—$O_2{}^{1-6}$ AT 25°C
(Electrolyte $1N$ KOH)

Metal	Amperes per square centimeter				
	0.001	0.01	0.1	0.5	1.0
Copper..................	0.42	0.58	0.66	0.74	0.79
Gold....................	0.67	0.96	1.24	1.53	1.63
Graphite...............	0.53	0.9	1.09	1.19	1.24
Nickel, smooth....... ...	0.35	0.52	0.73	0.82	0.85
Nickel, spongy...........	0.41	0.56	0.69	0.74	0.76
Platinum, platinized......	0.40	0.52	0.64	0.71	0.77
Platinum, smooth........	0.72	0.85	1.28	1.43	1.49
Silver..................	0.58	0.73	0.98	1.08	1.13

[1] KNOBEL, *J. Am. Chem. Soc.*, **46**, 2613 (1924).
[2] KNOBEL, *J. Am. Chem. Soc.*, **46**, 2751 (1924).
[3] KNOBEL, CAPLAN, and EISEMAN, *Trans. Am. Electrochem. Soc.*, **43**, 55 (1923).
[4] KNOBEL and JOY, *Trans. Am. Electrochem. Soc.*, **44**, 443 (1923).
[5] NEWBERY, *J. Chem. Soc.* (London), **105**, 2419 (1914).
[6] NEWBERY, *Trans. Faraday Soc.*, Part I, **15**, 126 (1919).

Oxygen Overvoltage. In a manner similar to hydrogen overvoltage, oxygen overvoltage exists in the course of anodic evolution of oxygen. Only the noble metals, and a few others such as those of the iron group which can be "ennobled," can be satisfactorily employed for the evolution of oxygen. A table of values is given, Table 8, condensed from Knobel's tables in the

[5] GOODWIN, H. M., and KNOBEL, M., *Trans. Am. Electrochem. Soc.*, **37**, 617 (1920).

"International Critical Tables," McGraw-Hill Book Company, Inc., by permission.

TABLE 9. OVERVOLTAGE—$Cl_2{}^{1-6}$ AT 25°C
(Electrolyte Saturated Solution NaCl or KCl)

	Amperes per square centimeter				
	0.001	0.01	0.1	0.5	1.0
Graphite	.....	. ....	0 25	0.42	0.5
Platinum, platinized.... .	0.006	0.016	0.026	0.05	0.08
Platinum, smooth........	0.008	0.03	0.054	0.16	0.24

OVERVOLTAGE—$Br_2{}^{1-6}$ AT 25°C
(Electrolyte Saturated Solution NaBr or KBr)

	Amperes per square centimeter			
	0.01	0.1	0.5	1.0
Graphite..	.....	0 002	0.027	0.16	0.33
Platinum, platinized......	.. ...	0 002	0.012	0.07	0.2
Platinum, smooth	.....	0.002	.....	0.26	0.4

OVERVOLTAGE—$I_2{}^{1-6}$ AT 25°C
(Electrolyte Saturated Solution NaI or KI)

	Amperes per square centimeter			
	0.01	0.1	0.5	1.0
Graphite................	.....	0 013	0.1	0.4	0.8
Platinum, platinized......	.....	0.006	0.03	0.09	0.2
Platinum, smooth........	.....	0.004	0.03	0.12	0.22

[1] KNOBEL, *J. Am. Chem. Soc.*, **46**, 2613 (1924).
[2] KNOBEL, *J. Am. Chem. Soc.*, **46**, 2751 (1924).
[3] KNOBEL, CAPLAN, and EISEMAN, *Trans. Am. Electrochem. Soc* . **43**, 55 (1923).
[4] KNOBEL and JOY, *Trans. Am. Electrochem. Soc.*, **44**, 443 (1923).
[5] NEWBERY, *J. Chem. Soc.* (London), **105**, 2419 (1914).
[6] NEWBERY, *Trans. Faraday Soc.*, Part I, **15**, 126 (1919).

In the case of oxygen overvoltage, Foerster[6] has shown that oxides may be supposed to form on the surfaces of anodes. The general phenomenon of oxygen overvoltage can be accounted

[6] FOERSTER, F., *Z. physik. Chem.*, **69**, 236 (1909); *Z. Elektrochem.*, **16**, 353 (1910); "Elektrochemie wässeriger Lösungen," pp. 335–341, J. A. Barth, Leipzig, 1923.

for if it be assumed that an increasing oxygen concentration at the electrode surface will cause an increasingly positive potential.

Halogen Overvoltage. Overvoltages for the halogens exist of a nature comparable to hydrogen and oxygen overvoltages. On continued electrolysis these frequently attain very large values. Values for chlorine, bromine, and iodine overvoltages are given in Table 9, condensed from Knobel's tables in the "International Critical Tables," McGraw-Hill Book Company,

Inc., by permission. For a more complete discussion, the reader is referred to the work of Müller,[7] Luther and Brislee,[8] Pfleiderer,[9] and Foerster and Tenne.[10]
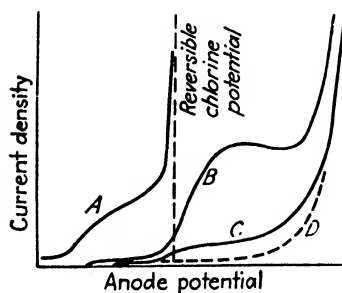
The H^+ ion concentration or the pH of a solution may markedly affect chlorine overvoltage. Reference should be made to Fig. 7. With platinized platinum in a solution of N NaCl containing $0.01N$ NaOH, curves such as A

FIG. 7. Current density-chlorine overvoltage relation.

are obtained, whereas in N HCl with smooth platinum, curve B results which is to be compared with the vertical line of the reversible chlorine potential. Curve C corresponds to A but with smooth platinum as the electrode. As in hydrogen and oxygen evolution, chlorine deposition may be presumed to involve the formation of monatomic chlorine within the electrode surface material. Solubility of molecular chlorine in the electrolyte may affect the chlorine overvoltage. In commercial practice electrolytes are maintained for minimum chlorine solubility.

Inasmuch as OH^- ions may discharge at the anode along with chlorine ions, the oxygen overvoltage of the particular electrode may become important. With changes in current density, increases in OH^- ion and oxygen at the electrode interface may become great enough that potentials will be reached at which oxygen is evolved. The lower the voltage at which OH^- ion

[7] MÜLLER, E., *Z. Elektrochem.*, **6**, 573 (1900); **8**, 426 (1902).

[8] LUTHER, R., and BRISLEE, F. J., *Z. physik. Chem.*, **45**, 216 (1903).

[9] PFLEIDERER, G., *Z. physik. Chem.*, **68**, 49 (1909).

[10] FOERSTER, F., and TENNE, A., Dissertation, Dresden (1913); *Z. Elektrochem.*, **22**, 86 (1916).

may be discharged at the particular electrode, the greater will be the effect of oxygen on the chlorine reactions.

The effects of oxygen, pH, and other factors at platinum and graphite electrodes have been studied by Boericke[11] and Foerster and Yamasaki[12] for bromine deposition and by Foerster and Herrschel[13] for iodine.

Theories of Overvoltage. For an extensive discussion of the theories of overvoltage, the reader is referred particularly to the work of Foerster,[14] Newbery,[15] Möller,[16] Tafel,[17] MacInnes,[18] Haber,[19] and Glasstone.[20] One theory which finds considerable acceptance supposes that overvoltage is due to an increase in the electrolytic solution pressure, as given in the Nernst equation, by the formation of a hydride with the metal of the electrode with greater free energy content than gaseous hydrogen. Hydrogen at atmospheric pressure dissolves to an appreciable extent in most metals to form some sort of alloy with the metal. It is well known that hydrogen is dissolved by metals of the platinum group to such an extent that the resulting electrode is of the gas type and is commonly referred to as a "hydrogen electrode." Anodic overvoltage in a similar manner would be due to oxides or adsorbed oxygen. As solid solutions, these oxides and hydrides would generate reverse emfs at the anode and cathode and be assumed to account for high oxygen and hydrogen overvoltage.

Polarization and Metal Deposition. Processes involving cathodic metal deposition usually take place almost reversibly. In the majority of cases small polarizations are all that are required. This is essentially of the concentration polarization type. In electrolysis of solutions containing complex metallic

[11] BOERICKE, F., *Z. Elektrochem.*, **11**, 57 (1905).

[12] FOERSTER, F., and YAMASAKI, J., *Z. Elektrochem.*, **16**, 321 (1910).

[13] FOERSTER, F., and HERRSCHEL, F., *Z. Elektrochem.*, **22**, 89 (1916).

[14] FOERSTER, F., "Elektrochemie wässeriger Lösungen," J. A. Barth, Leipzig, 1923.

[15] NEWBERY, E., *J. Chem. Soc.* (London), **105**, 2419 (1914); **109**, 1107, 1359 (1916).

[16] MÖLLER, H. G., *Z. physik. Chem.*, **65**, 226 (1909).

[17] TAFEL, J., *Z. physik. Chem.*, **34**, 200 (1900).

[18] MacINNES, D. A., *J. Am. Chem. Soc.*, **41**, 194 (1919).

[19] HABER, F., *Z. Elektrochem.*, **8**, 539 (1902).

[20] GLASSTONE, S., *Trans. Chem. Soc.* (London), **125**, 250 (1924).

ions, considerable polarization may be met even at small current densities.

Particularly in the case of metals of the iron and nickel group, appreciable polarization may be encountered even in the electrolysis of simple salt solutions. Table 10 shows the relation between cathodic potentials of iron from slightly acid $FeSO_4$ solutions and those of copper deposition from $CuSO_4$ solutions, both at 20°C, as obtained by Foerster and Mustad.[21] The difference in the behavior of the two salts is very marked.

TABLE 10

Current density	$CuSO_4$, volts	Over-voltage	$FeSO_4$, volts	Over-voltage
0.00	+0.303	......	−0.465	
0.57 × 10⁻⁴ amp, per cm ²	......	......	−0.573	−0.108
1.13	+0.292	−0.011	−0.594	−0.129
2.27	+0.290	−0.013	−0.606	−0.141
4.5	+0.289	−0.014	−0.616	−0.151
11.3	+0.287	−0.016	−0.630	−0.165
22.7	+0.281	−0.022	−0.644	−0.179

Nickel and cobalt salts behave in a manner similar to that of iron. Large polarization values are met in the deposition of chromium and manganese. In the case of chromium, the energy efficiency of chromium deposition is quite low, inasmuch as the evolution of hydrogen is the major cathodic process. With chromium and manganese, anodic solution does not proceed easily, passivity may readily set in, and OH^- ion discharge with oxygen evolution become the more important anode process with increases of current density and anode potential. Zinc, which is baser than iron or nickel, deposits reversibly even at high current density, a factor which is of great industrial importance in zinc electrowinning. The large polarizations met in iron deposition are associated with the evolution of hydrogen and its adsorption by the freshly deposited metal. This hydrogen adsorption markedly changes the electrode potential. If the hydrogen be "baked out," the electrode potential will, under the same set of conditions, show a different value.

If the deposited metal form an alloy with the electrode, it is

[21] FOERSTER, F., and MUSTAD, O., *Abhand. Bunsen Ges.*, **2**, 44 (1909).

obvious that new electrode potentials will then be involved with different polarization values for the particular set of circumstances. The rate of alloying will be affected by diffusion into the body of the electrode, and this factor will cause the polarization values to change.

With liquid cathodes, diffusion and alloy formation can proceed more rapidly. The electrode surface is changed, and the original electrode potentials and polarization values no longer control. At the beginning, the hydrogen overvoltage in a mercury cell at which Na^+ ions are being discharged is high, but with alloy formation taking place, the hydrogen overvoltage may be decreased under the new set of conditions, so that with sodium-rich amalgams H^+ ion deposition is the major process. With continuance of hydrogen evolution, the amalgam may lose sodium, with corresponding increase in hydrogen overvoltage so that Na^+ ion discharge in turn may displace hydrogen evolution.

Hydrogen Overvoltage and Metal Deposition. The electrode potential of a cathode must be represented by the equation

$$e_m = \frac{RT}{nF} \log \frac{p_m}{P_m} + o_m$$

and

$$e_h = \frac{RT}{F} \log \frac{p_h}{P_h} + o_h$$

Fig. 8. Overvoltages of hydrogen and of metal, showing conditions for deposition of metal alone.

where o_m is the overvoltage for the metal deposition. If e_h be more negative than e_m for all current densities, only metal will deposit. The c.d.-voltage curves will then be related as shown in Fig. 8. As long as the limiting current density for the metal is not exceeded, the relations shown in the curve apply to metals that are more noble than hydrogen in strongly acid solutions. If the limiting current density be exceeded, hydrogen must deposit. The potential of the electrode will then jump over to the hydrogen curve.

If for all current densities e_h be less negative than e_m, only hydrogen will be deposited. The curves in the figure will then be interchanged. This applies to those metals which decompose water.
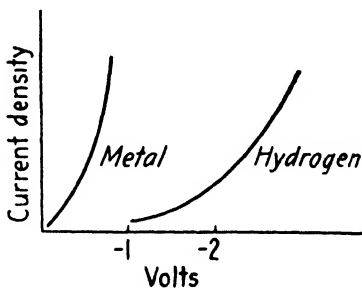
Reductions of the H^+ ion concentration through the use of neutral solutions are not of aid in attempted deposition of metals such as aluminum and magnesium.   Even if only a small amount of hydrogen be liberated, the solution around the cathode becomes alkaline and hydroxides are precipitated on its surface.   Tucker and Thomssen[22] find that small amounts of aluminum can be deposited from saturated $AlCl_3$ solutions at high current density at cathodes rotating at 15,000 rpm.

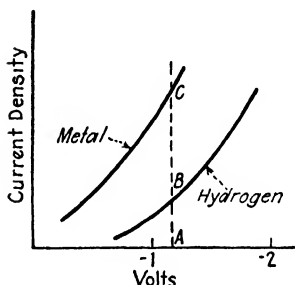Metal and hydrogen will be deposited together if $e_h = e_m$.

Fig. 9.   Overvoltages of hydrogen and of metal, showing conditions for simultaneous deposition of metal and hydrogen.

The c.d.-voltage curves would then be related as in Fig. 9, where the relative positions of the hydrogen and the metal curves are such that the same vertical line cuts both of them.   The amounts deposited at a given electrode potential will be proportional to the current density corresponding to the intersections of the vertical and the metal and hydrogen curves, and the efficiency of metal deposition is $AC/(AC + AB)$. Nickel, zinc, and cadmium belong to this case.   It is to be noted that in the case of metals that tend to dissolve in acid, the current cannot go in the direction from solution to cathode; consequently hydrogen cannot be deposited until the impressed voltage is at least equal to that with which the metal tries to dissolve.

Aqueous solutions always contain H^+ and OH^- ions which, depending upon the electrical conditions, may remain in the electrolyte in equilibrium or be discharged in preference to other ions, or other ions may be discharged in preference to them. With the noble metals whose single electrode potentials are more positive than that of hydrogen, the metals are deposited in preference to hydrogen at low current density.   With high current density, voltage values may be reached at which there is simultaneous deposition of the metal and hydrogen.   On the other hand, very base metals whose single electrode potentials are very much more negative than that of hydrogen, examples

[22] Tucker, S. A., and Thomssen, E. G., *Trans. Am. Electrochem. Soc.*, **15**, 497 (1909).

of which are the alkaline and the alkaline earth metals, are not cathodically deposited from aqueous solutions. Only hydrogen evolution occurs. Theories have been proposed involving the deposition of these metals and discharge of their ions with immediate chemical reaction with water and the formation of hydrogen. From the electrochemical viewpoint, the theory is questionable.

For the common metals such as lead and tin, the iron group, zinc and cadmium, in order to make any predictions, it is necessary to consider the single electrode potentials of the metal and hydrogen in the particular solution, the relative positions of the c.d.-cathode potential curves for the metal and hydrogen, and the slopes of these curves. Often the chemical rate of solution of the deposited metal is a controlling factor. Zinc may be and iron may not be deposited on the cathode from a highly acid sulfate solution with high current efficiency.

At the beginning of electrolysis involving metal deposition, the original cathode and the hydrogen overvoltage at this cathode will be an important factor as to whether hydrogen or metal is to be deposited, either singly or together. If, however, the metal surface become coated with deposited metal, a new set of controlling conditions is involved. Inasmuch as the hydrogen overvoltage increases sharply with increase in current density, metal deposition is thus favored at high current density and high metal ion concentration. Increase in temperature reduces hydrogen overvoltage and favors H^+ ion deposition.

Metals of the iron group show low hydrogen overvoltage at ordinary current density. Deposition of the metals is most effective in electrolytes of high metal ion concentration and at low current density. At higher current density, hydrogen evolution with saturation of the metal and changes in the single potential of the cathode becomes the more important reaction. Manganese, which has a high hydrogen overvoltage similar to zinc, differs from this metal in that it requires a high polarization like iron for its cathodic deposition.

When hydrogen evolution as the result of H^+ ion deposition becomes the major or an important part of the cathodic deposition process, the electrolyte in the region of the cathode may become alkaline, and insoluble hydroxides of the metal ions may be precipitated. In many industrial processes, agents are added

to the electrolyte as buffers to maintain the pH of the electrolyte with the avoidance of alkaline areas.

Deposition of Alloys. Codeposition of two metals may occur when their equilibrium potentials in a given electrolyte are very close. It is to be understood that the electrode potentials, and as a result the relative positions of the metal ions in relation to each other, may be markedly different with different anions. Single electrode potential tables or electrochemical series may not have the same order with acetates, cyanides, chlorates, or other anions as with sulfates, in connection with which the values are usually determined. Deposition potentials of the metals from complex electrolytes, where the metal ion is not produced as the result of primary but of secondary ionization, are factors in the possibility of alloy deposition.

Alloys may also be deposited when there is considerable depolarization of the baser metal deposition. Codeposition may also take place at current densities which are so high that diffusion of the ions of the nobler metal is not rapid enough to maintain this current density. The two metals then deposit at different efficiencies. Simultaneous deposition may also take place if the nobler metal be highly polarized at moderate current density. The entire subject of simultaneous deposition of two metals will be discussed more completely in its practical aspects under electroplating.

Effect of Alternating Current on Electrolysis. Electrochemical literature shows that by superimposing an alternating current on direct current in electrolysis, a decrease in electrode potential is obtained. This is manifested by measurements of overvoltage and by the character of the products from electrolysis, more of the intermediate products and less of the end products being obtained. Since the exact cause of overvoltage is not well understood and since methods of properly measuring it are in some respects doubtful, it is obvious that it would be difficult to make similar measurements with combined alternating current and direct current. Some literature has reported negative overvoltages under such circumstances, which at once opens the question as to the suitability of the method employed.

Overvoltage exists only while current flows, so that to obtain correct values current should be flowing when measurements are made. Such a measurement always involves a potential

caused by resistance of the solution, resistance of the electrode, and any resistance which may exist between the solution and the electrode by virtue of the liberation of gas. These extraneous potentials have been eliminated by extrapolation or by momentarily breaking the circuit and measuring the back emf as the overvoltage. These methods have not been applied in using a superimposed alternating current on direct current.

The amounts of electrochemical effects of alternating current alone are dependent on current density, those of superimposed alternating current on the ratio of the alternating to the direct component of the current, while the effects of both types of current are greatly influenced by the frequency. Experimental work shows that the superposition of an alternating current on a d.c. electrode process tends to reduce any irreversibility in that process. Superimposed alternating current acts as a depolarizer. It reduces anode and cathode polarization and electrochemical passivity. Chemical depolarizers may leave undesirable decomposition products in the electrolyte, but superimposed alternating current will not. Superposition results in marked reduction of oxygen overvoltage and electrochemical passivity of anodes. Cocks[23] has noted effects in nickel plating and in combined zinc and nickel plating from a feebly acid solution of zinc and nickel sulfates. Superposition of alternating current assists the anodic solution of chromium in acid and alkali solutions. The only case of the technical use of superimposed alternating current in electrolysis is that of the Wohlwill modified gold-refining process.[24] The introduction of the alternating current in the Wohlwill process converted it from a laboratory curiosity to a commercial success. The sole effect of the alternating current was on the solution of the anode. Recent proof of the desirability of the presence of chlorides in nickel plating baths and of the employment of temperatures of 30 to 50° tends to discount the outstanding advantages of superimposed alternating current.

Superimposed alternating current reduces the hydrogen overvoltage as determined by Goodwin and Knobel[25] with platinum, lead, mercury, and copper in normal H_2SO_4 at frequencies from

[23] Cocks, H. C., *Metal Ind. (London)*, **34**, 396–398, 414, 424–425 (1929).

[24] Wohlwill, E., British Patent 6,276 (1909).

[25] Goodwin, H. M., and Knobel, M., *Trans. Am. Electrochem. Soc.*, **37**, 617 (1920).

3 to 100 cycles per sec.   Grube and Dulk[26] obtained similar
results for oxygen, and Puri[27] for chlorine.   Hydrogen was
liberated at potential values more positive and oxygen at values
more negative than the corresponding reversible figures.   Anodic
metal solution is affected by alternating current, in that the anode
corrosion is increased.   Coppadoro[28] and Marsh[29] state that
nickel dissolves in solutions which it ordinarily resists, and
platinum may pass into solution in KCN.

Jones[30] finds that in the electrolysis of H_2SO_4 with lead elec-
trodes, the maximum overvoltage obtained during cathodic
action is only slightly lowered by superimposing increasing
amounts of alternating current upon direct current.   If the metal
be one which normally becomes passive at higher current density,
the use of superimposed alternating current tends to preserve
the active condition and raises the limiting current density at
which metal solution ceases.   Examples are given by gold in
chloride solutions,[31] by platinum in various electrolytes,[32] by
iron and lead in alkaline solutions,[33] and by nickel in various
neutral or faintly acid solutions.[34]

In electrolytic oxidation processes the use of superimposed
alternating current lowers the oxidizing potential and thus can
markedly influence the nature of the anodic reaction, with the
production of intermediate compounds which under ordinary
conditions would be converted into others of a more highly
oxidized nature.

Primary cells which show considerable polarization will have
higher emfs if alternating current be passed through,[35] while those
cells which operate nearly reversibly will not be so affected.[36]

[26] GRUBE, G., and DULK, B., *Z. Elektrochem.*, **24**, 237 (1918).

[27] PURI, V. S., Thesis, London, 1923.

[28] COPPADORO, A., *Gazz. chim. ital.*, **36**, ii, 693 (1906).

[29] MARSH, S., *Proc. Roy. Soc. (London)*, **97A**, 124 (1920).

[30] JONES, W. B., *Trans. Am. Electrochem. Soc.*, **41**, 151 (1922).

[31] WOHLWILL, E., *Z.Elektrochem.*, **16**, 25 (1910); PURI, V. S., *op. cit.*

[32] RUER, R., *Z. Physik. Chem.*, **44**, 81 (1903).

[33] GRUBE, G., and GMELIN, H., *Z. Elektrochem.*, **26**, 153 (1920); GRUBE, G.,
Z. Elektrochem., **28**, 275 (1922).

[34] TUCKER, S. A., and LOESCH, H. G., *J. Ind. Eng. Chem.*, **9**, 841 (1917);
KOHLSCHÜTTER, V., and SCHÖDL, H., *Helv. Chim. Acta*, **5**, 490 (1922).

[35] BROWN, S. G., *Proc. Roy. Soc. (London) A.*, **90**, 26 (1914); GHOSH, J. C.,
J. Am. Chem. Soc., **36**, 2333 (1914); PURI, V. S., Thesis, London, 1923.

[36] GHOSH, J. C., *op. cit.*

Tucker and Loesch[37] have, however, suggested the application of alternating current in the case of nickel plating in order to increase the rate of solution of the anodes.

As to the theory of depolarizing action of alternating current, little can be said at the present, although it is expected that by the use of instruments such as the oscillograph and high-frequency apparatus, some basic understanding will eventually be reached.[38] The industrial application of superimposed alternating current on direct current used for electrolysis has had little development, but it is expected, particularly in the field of electroorganic chemistry, to find increasing application.

Inasmuch as overvoltage commercially means that increased voltages must be applied to maintain electrolysis, greater quantities of energy must be expended. Continuous attention in commercial plants is given to contacts to eliminate ohmic resistance, and to electrode materials, electrode surfaces, current densities, and related factors to maintain overvoltage values as low as possible. It follows that with different electrode materials different overvoltages may be needed, and the type of electrode process may be controlled by the proper selection of electrode material and its overvoltage for the particular gas or electrolytic product in question.

[37] TUCKER, and LOESCH, *loc. cit.*

[38] See the views of RUER, R., GHOSH, J. C., GOODWIN, H. M., and KNOBEL, M., *op. cit.;* BROCHET, A., and PETIT, J., *Z. Elektrochem.*, **10**, 909 (1904); **11**, 441 (1905); ARCHIBALD, E. H., and VON WARTENBERG, H., *Z. Elektrochem.*, **17**, 812 (1911); REITLINGER, O., *Z. Elektrochem.*, **20**, 261 (1914); BANCROFT, W. D., *Trans. Am. Electrochem. Soc.*, **29**, 309 (1916); GRUBE, G., *Z. Elektrochem.*, **24**, 237 (1918); GRUBE, G., and METZGER, H., *Z. Elektrochem.*, **29**, 100 (1923).

Part II

TECHNICAL ELECTROCHEMISTRY

.

CHAPTER 6

ELECTROCHEMICAL ANALYSIS

Electrochemical methods are employed to a considerable extent in analytical work for the determination of metals from solution, and for the separation of these metals one from the other by deposition at controlled voltages. From the analytical viewpoint, electrochemical analysis employs gravimetric methods in that the precipitate formed by electrical action is weighed on an analytical balance. While the electrolysis of a simple salt may be considered as a well-understood process, the practical accomplishment of such a process for the purpose of a quantitative analysis is usually possible only when a certain set of conditions is maintained. As a function of the salt to be used, the solvents, temperature, voltage, current density, and the nature and kind of electrode, deposition may or may not occur upon passage of a current; the deposit may be contaminated by other products of electrolysis; or it may not have the proper physical character for convenient quantitative handling, in that it shows lack of adherence to the electrode and crumbles or dusts off during the electrolysis or during the process of washing.

Electrolytic methods are more frequently applied to the determination of metallic ions than of nonmetals, although methods exist and have been perfected for the determination of the latter. In specific cases certain anions must be excluded because they yield substances that attack the anode or because the acids produced by electrolysis affect the desirable physical form of the deposit. Chloride electrolysis with the formation of chlorine at a platinum anode is undesirable because of the corrosive effect on the anodes. Experimental work has shown that often certain substances exert a very important influence on the physical character of the deposited metal. Such materials are added to the electrolyte for this reason, although from other viewpoints they may be objectionable. For example, in the electrolysis of $CuSO_4$ solution, HNO_3 causes a deposit of firm

bright red and adherent metal, while the electrolysis of the $CuSO_4$ without additions gives a dark red or brown deposit of finely divided copper which is liable to dust off and be lost during washing.   Silver salts are best electrolyzed in the absence of HNO_3.   Electrolysis is caused to take place in double cyanide baths where firm white deposits are obtained, in preference to the electrolysis of $AgNO_3$ where crystalline, easily detached precipitates are formed. In all electroanalytical work, current and energy consumptions are relatively unimportant.   The form of deposit, its quantitative precipitation and suitability for handling, washing, and weighing are all important.

A common misconception is the belief that additions of other electrolytes to solutions to be electrolyzed are made in order to increase the conductivity of the solution.   The addition of a foreign electrolyte can increase the conductivity of the main electrolyte only by itself acting as a carrier of current.   In this case it has accomplished no desirable effect, since the prime object is to make the minimum current do the maximum work in discharging the ion already in solution.

Relatively little work has been done in the development of electrochemical methods for analytical work employing solvents other than water.   The processes are usually carried out at laboratory temperatures.   Electrolysis is caused to take place at controlled voltages whose values have been determined by experiment and are the practical decomposition voltages of the solutions, which include many factors such as anodic and cathodic overvoltages, temperatures, solution resistance, effective added electrolytes. etc.   Sand[1] proposed the analytical separation of metals by properly grading the cathode potential difference. Current densities employed are usually low so that the most desirable form of cathode deposit may be obtained.   Such low current densities have the disadvantage that they necessitate somewhat long periods of time for the completion of the electrolysis.   In order to shorten this time, gauze electrodes, rotating anodes, and rotating cathodes are employed, by the use of which higher current density may be used without the production of undesirable forms of deposit.   In other cases mercury cathodes which absorb metals of the salt solution being electrolyzed are

[1] SAND, H. J. S., *J. Chem. Soc.*, **91**, 373 (1907).

advantageous. For specific methods reference should be made to the standard works on analytical chemistry.

Measurement of Hydrogen Ion Concentration. The electrochemical measurement of acidity or alkalinity in industrial processes by either intermittent methods or continuous ones, results of which are recorded by indicating or recording instruments, is basic for the control of large numbers of industrial operations. A brief discussion of H^+ ion measurement is included at this point.

The concentration of H^+ ion in any solution may be expressed in terms of the normal H^+ ion solution containing 1 g of H^+ ion per liter. In most solutions the H^+ ion concentration is only a small fraction of that in a normal solution and is expressed as powers of 10 in order to avoid decimals with a large number of ciphers or fractions with large denominators. A concentration of 0.0001 g H^+ ion per liter thus becomes $1/10^4$ or 1×10^{-4}. The symbol pH is used to designate the logarithm of the reciprocal of the H^+ ion concentration, or the negative log of the H^+ ion concentration. Thus a $0.0001N$ solution of H^+ ion equals 1×10^{-4} or $-\log (H^+) = 4 = \log (1/H^+)$; therefore pH = 4. Concentrations that are uneven decimal fractions of normal can also be expressed in pH units. Thus for a solution in which the concentration is $2.73 \times 10^{-4} N$, the pH number is 3.566. This can be proved by the use of a logarithm table, which shows that $\log 2.73 = +0.434$ and $\log 10^{-4} = -4.000$. Since the numbers are to be multiplied, the logs are added; hence $-4.000 + 0.434 = -3.566$. Therefore $\log (H^+) = -3.566$, so $-\log (H^+) = 3.566$ and pH = 3.566.

If it be desired to know the actual figure for H^+ ion concentration when only the pH value is given, it can be found by the reverse of the calculation just given. Thus 9.63 pH means that $(H^+) = 1 \times 10^{-9.63}$. The exponent $-9.63 = -10 + 0.37$; hence $10^{-9.63} = 10^{-10} \times 10^{+0.37}$. The log table shows that the exponent 0.37 corresponds to the number 2.34. Therefore $(H^+) = 10^{-9.63}$ is the same as $(H^+) = 2.34 \times 10^{-10}$.

In a similar manner the alkalinity of a base may be expressed as pOH = $\log [1/(OH^-)]$. In an acid-base equilibrium water is formed and neutrality is reached when $[(H^+) \times (OH^-)]/(HOH) = K$. The number of water molecules dissociated is so small in comparison that the concentration HOH may be

considered as constant and combined with K, making the equation $(H^+) \times (OH^-) = K(HOH) = Kw$. At 25°C, Kw is 10^{-14} which is the product of the concentration of the H^+ ions and OH^- ions which are equal to each other, so that the concentration of each is 10^{-7} and in water pH = 7. In an acid solution the concentration of H^+ ions is greater than that of water, owing to the dissociation of the acid and according to its dissociation constant. In an analogous manner in basic solutions the OH^- ion concentration is greater than that of water. But since water is present, there must be some OH^- ions in any acid solution and some H^+ ions in any basic solution, the concentration of one of these varying inversely with the concentration of the other and the product of the two concentrations being equal to 10^{-14}. Then $(H^+)(OH^-) = 10^{-14}$ and $\log[1/(H^+)] + \log[1/(OH^-)] = 14$, and pH + pOH = 14.

It is evident that if the concentration of either ion is known, that of the other can be computed, so that the reaction of any solution, whether acid, alkaline, or neutral, can be expressed in terms of pH. An acid-alkaline scale can be set up in terms of H^+ ion concentrations with a pH = 0 at one end representing a normal H^+ ion solution, and a pH = 14 at the other end representing the H^+ ion concentration of a normal OH^- ion solution. Any pH number from zero to 7 thus indicates acidity with decreasing acidity as the number increases. pH 7 indicates neutrality and any pH number between 7 and 14 indicates an alkaline solution with increasing alkalinity (or decreasing acidity) as the number increases.

H^+ ion concentration in a water solution can be determined electrically by the use of two hydrogen electrodes in contact with the solution and the voltage developed by the two electrodes determined by the use of a potentiometer. Such a setup is shown in Fig. 10. From the following formulae the H^+ ion concentration or pH can be calculated.

$$\frac{V}{0.0001983T} = \log \frac{Cn}{C}$$

where T is the absolute temperature, V the voltage, Cn the known concentration, and C the unknown. At 25°C for the temperature of the two solutions, the equation becomes

$$\frac{V}{0.0591} = \log \frac{Cn}{C}$$

If the known solution be a normal H^+ ion solution, then $Cn = 1$ and $\log 1/C = \mathrm{pH}$, and the equation becomes

$$\frac{V}{0.0591} = \mathrm{pH}$$

A more convenient arrangement substitutes a calomel electrode for one of the hydrogen electrodes, as a result of which the
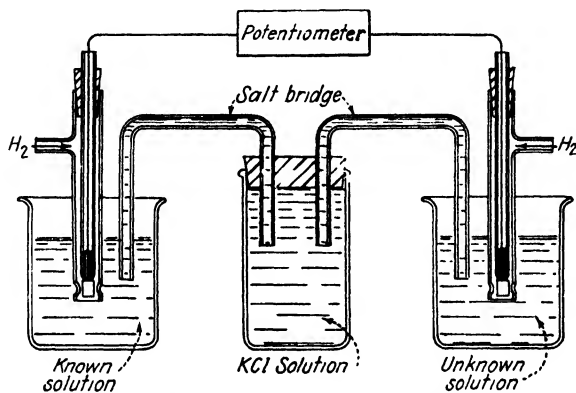

Fig. 10.   Theoretical H^+ ion concentration setup.

arrangement becomes that of Fig. 11 (p. 94).   The formula then becomes

$$\frac{V - v}{0.0591} = \log \frac{1}{C} = \mathrm{pH}$$

The potential of the calomel electrode varies with its temperature as well as with the KCl concentration, as shown in Table 11.

TABLE 11

Calomel electrode	Potential at 20 deg C	Potential at 25 deg C	Potential at 30 deg C
Tenth normal............	0.3379	0.3376	0.3371
Normal.................	0.2860	0.2848	0.2835
Saturated...............	0.2496	0.2458	0.2420

Quinhydrone Electrode.   For many practical purposes in industry the quinhydrone electrode is substituted for the hydro-

gen electrode. The basis of this electrode is a piece of platinum
or gold exactly the same as used for the hydrogen electrode, but
the surface of the metal is not platinized, and it is not supplied
with gaseous hydrogen. Instead a small quantity of quinhydrone
(benzoquinhydrone) is dissolved in the solution, and within cer-
tain pH ranges the electrode in the solution acquires a potential
that is definitely related to the H^+ ion concentration of the
solution. The potential is measured against that of a calomel
electrode, and the pH value is found from the measured voltage
in the same manner as with a hydrogen electrode. Quinhydrone
is so slightly soluble in acid that only small quantities are neces-
sary to saturate the solution. In solutions more alkaline than
pH 8, quinhydrone is more soluble, dissociates, and becomes
oxidized. The quinhydrone electrode potential is altered to such
an extent that the measured voltage is no longer a linear func-
tion of pH. The quinhydrone electrode is therefore not suitable
for use in decidedly alkaline solutions.

The relation of voltage to pH is given by the expression

$$\text{pH} = \frac{0.7177 - 0.00074t - V - v}{0.0001983T}$$

where t is the temperature of the solution and the electrodes,
V the measured voltage, v the correction factor for the potential
of the calomel electrode, and T the absolute temperature. With
a saturated calomel electrode at 25°C, $v = 0.2458$ and the equa-
tion becomes

$$\frac{0.453 - V}{0.0591} = \log \frac{1}{(H^+)} = \text{pH}$$

Glass Electrode. The electrode itself consists of a thin-
walled glass bulb which is blown on the end of a glass tube, the
bulb and tube being filled with HCl adjusted to a pH = 1. The
electrode terminal is formed by a quinhydrone electrode in this
solution. This quinhydrone reference electrode is easy to pre-
pare, is reproducible, and is stable. The pH indications given
by the assembly as described are the result of the direct transfer
through the glass bulb which is a conductor. The bulb is quite
thin, being of the order of 0.001 mm. The composition of the
glass is rather critical and that recommended by MacInnes and

Dole[2] (72 per cent SiO_2, 22 per cent Na_2O, and 6 per cent CaO) finds wide acceptance. Voltage measurements are made between the inner quinhydrone electrode and a calomel reference electrode immersed in the test solution in the manner described previously. The resistance of the glass electrode in the forms available is from 2 to 6 megohms, so that high sensitivity galvanometers must be employed.

Antimony Electrode. This electrode consists of a small block of specially prepared antimony metal with its end exposed to the test solution. In use, it is necessary that the solution be in motion and exposed to the open air. The electrode has a low resistance, shows rapid response to the pH changes, and is rugged. It finds wide commercial acceptance in continuous pH measurements and control of a wide variety of industrial materials. While each of the other measuring electrodes follows a definite voltage-pH curve, the antimony electrode follows one of several curves whose shapes depend upon the nature and concentration of the substances in the solution being tested. The curves are identical below pH 5 and above pH 10. Within this range the electrode for the specific solutions under test needs to be calibrated.

The characteristics of the various measuring electrodes for pH and H^+ ion control are given in Table 12. MacInnes and Longworth[3] have described the glass electrode in detail, and Perley[4] has compared various electrode systems for industrial control.

Potentiometric Titration. The changes occurring in a solution as the result of the addition of a reagent to that solution may be followed in an electrochemical manner in terms of the voltage set up in a system with a measuring electrode. The voltage corresponding to pH 7 may be set as the neutral point. A typical arrangement of apparatus would be such as is shown in Fig. 11 but with the addition of a burette holding a specialized solution. A titration is made from the burette into the unknown solution. The general method is termed either "electrometric" or "potentiometric titration." It is free from the difficulties encountered

[2] MacInnes, D. A., and Dole, M., *Ind. Eng. Chem., Anal. Ed.*, **1**, 57 (1929).

[3] MacInnes, D. A., and Longworth, L. G., *Trans. Electrochem. Soc.*, **71**, 73 (1937).

[4] Perley, G. A., *Trans. Am. Inst. Chem. Engrs.*, **29**, 257 (1933).

TABLE 12. CHARACTERISTICS OF MEASURING ELECTRODES[1]

Measuring electrode	Useful range pH	Limit of error pH	Range of resulting e.m.f.[2] volts	General characteristics	Applications
Hydrogen Gas	0–14	±0.01	+0.25 to +1.10	High accuracy Applicable to whole pH range Not applicable in presence of dissolved gases, foaming solutions, oxidizing or reducing solutions Requires pure supply of hydrogen gas and freshly platinized surface No salt error	General research Calibration of buffer and colorimetric standard solutions and of other electrodes Biochemical investigations
Quinhydrone	0–9	±0.01	−0.45 to +0.10	Relatively inexpensive equipment required No catalytic metal surface or gas required Simplicity of operation Sample contaminated with quinhydrone Inapplicable to oxidizing and reducing solutions in general. Applicable to certain mild oxidizing systems Small salt errors	General research Biological solutions Industrial, such as nickel plating, water purification, dairy products, etc.
Glass	1–14	±0.1 in general ±0.02 if calibrated before and after test	−0.40 to +0.37 based on quinhydrone internal element	Independent of oxidation-reduction systems Only pH electrode adaptable to non-buffer solutions No contamination of sample Presence of sodium, potassium, or lithium salts causes appreciable error above 9 pH and 25°C High-resistance system Some forms susceptible to breakage	General research Colloidal solutions Tanning liquors Special adaptation in presence of highly oxidizing and reducing systems General plant and field testing

[1] Courtesy of Leeds & Northrup Company, Philadelphia, Pa.

[2] The sign of the potential difference is considered positive when a reading is obtainable with the calomel electrode connected to the positive terminal of the potentiometer.

TABLE 12. CHARACTERISTICS OF MEASURING ELECTRODES.[1]—(*Continued*)

Measuring electrode	Useful range pH	Limit of error pH	Range of resulting e.m.f.[2] volts	General characteristics	Applications
Antimony	4–11.5 in general	±0.2 in general ±0.05 if calibrated before and after test	±0.10 to ±0.68	Rugged No gas or catalytic surface required Possible continuous measurements in open nonmetallic tanks and channels Very slightly soluble in acid solutions E.m.f./pH relation somewhat dependent on nature of solution Erroneous results in oxydation-reduction systems and in solution containing even traces of copper and silver salts, and high concentrations of sodium salts	Industrial processes; sugar refineries, paper mills, water treatment, etc. Recording and controlling

[1] Courtesy of Leeds & Northrup Company, Philadelphia, Pa.
[2] The sign of the potential difference is considered positive when a reading is obtainable with the calomel electrode connected to the positive terminal of the potentiometer.

when indicators are employed in colored solutions. The end points are not masked by turbidity or other factors which normally interfere in the usual titration methods. It can be seen that the method may be employed for titration to any voltage corresponding to any pH.

A modification of the method employs the abrupt change in the voltage of the electrode when the end point is reached.   When a curve is plotted with either pH or voltage as the vertical ordinate and the cubic centimeters of the titrating standard solution
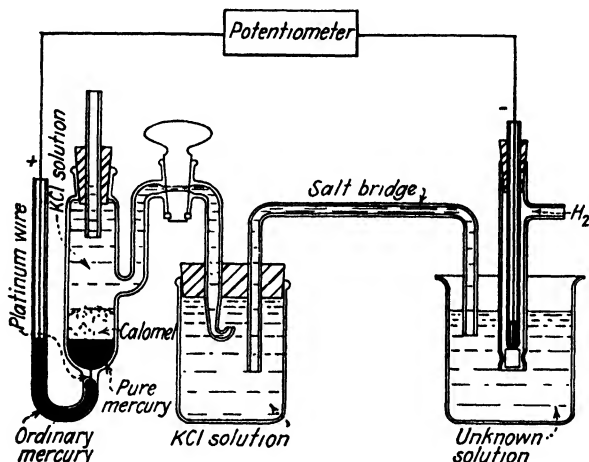

FIG. 11. H^+ ion concentration setup, substituting a calomel electrode for one of the hydrogen electrodes.

as the horizontal ordinate, there will be a change in the curve with a sharp vertical rise corresponding to a wide change in voltage or pH with a minimum addition of titrating agent.   This will be the end point of the titration.   In a similar manner, an oxidation-reduction reaction may be followed to its end point by plotting the emf against volume of standard solution and noting the abrupt change in voltage.   For specific methods in greater detail, reference should be made to the standard texts of analytical chemistry.[5]

[5] MAHIN, E. G., "Quantitative Analysis," McGraw-Hill Book Company, Inc., New York, 1932; RIEMAN, W., NEUSS, J. D., and NAIMAN, B., "Quantitative Analysis," 2d ed., McGraw-Hill Book Company, Inc., New York, 1942.

\/Conductance **Titration.** In the conductometric titration method, the abrupt change in the conductivity of the solution at the end point is used. It cannot be applied to as wide a range of determinations as the potentiometric method, inasmuch as the accuracy is affected by large amounts of electrolytes foreign to the particular reaction studied.

Control of trace materials by the usual chemical analytical methods is slow, tedious, and often difficult. Speed, together
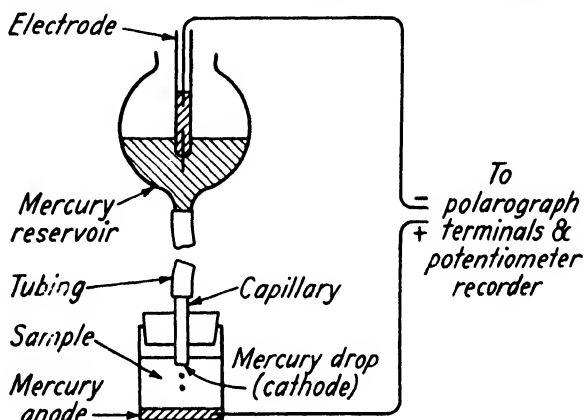
FIG. 12. Schematic illustration of dropping-mercury electrode used in polarograph.

with accuracy, accounts for the acceptance of the recording polarograph as an analytical tool.

Polarographic analysis[6] is based upon the method originated by Heyrovsky and Shikata based on current-voltage curves obtained with a dropping mercury cathode in a system containing a completely polarized electrode in conjunction with one which is not polarizable. A specialized measuring system needs to be employed for the regulation of the continuously renewed cathode surfaces and the automatic continuous re-solution of deposited substance at a minute cathode area that has a very high hydrogen overvoltage. Qualitative identification of the substances is established by voltage factors.

The dropping-mercury electrode, as shown in Fig. 12, consists of a fine-bore capillary tube connected by a neoprene tube to a

[6] MÜLLER, O. H., and BAUMBERGER, J. P., *Trans. Electrochem. Soc.*, **71**, 181 (1937).

mercury reservoir and placed in the solution so that very fine drops of mercury are formed beneath the surface. The rate of mercury flow may be adjusted by varying the height of the mercury reservoir and normally amounts to a drop every 1 to 3 sec. The mercury reservoir is connected to one terminal of the polarograph; the other cell terminal is a pool of mercury in the bottom of the solution vessel.

In operation, a few drops of mercury added to the sample act as one electrode of the cell. The dropping-mercury electrode is next inserted. An inert gas, usually nitrogen, is then bubbled through the solution to remove atmospheric oxygen which is reducible and gives a polarographic wave not usually of interest to the analyst. As the voltage impressed on the cell is slowly raised, the current remains nearly constant until a voltage is reached at which a component of the solution is reducible. The current then rises sharply to a new level, at which it remains constant until the voltage is reached at which a second component is reducible. Another sharp rise in current to a new constant value then occurs. These sharp rises in current are called "polarographic steps or waves."

The output from the polarographic cell may be fed to a recorder so that the displacement of the pen from zero is determined by the amount of current flowing through the cell. The chart is driven by a constant-speed synchronous motor. The polarographic bridge which supplies voltage to the cell is also driven by a synchronous motor, so that the chart displacement is a linear function of the voltage applied to the cell; *i.e.*, the time ordinate of the chart becomes, in essence, the voltage ordinate. The record obtained, therefore, is current *vs.* voltage, or a polarogram, a typical case of which is shown in Fig. 13.

To the analyst an important field of electrodeposition is at a controlled potential. The development of automatic equipment for making such determinations, which is peculiarly American, indicates that the method known since about 1906 will come into more general use, particularly in industrial laboratories. Lingane[7] has described a method for the determination of copper in copper-base and tin alloys in which relatively large amounts of tin, antimony, lead, and zinc do not interfere. Small amounts of iron, nickel, arsenic, and phosphorus may also be present.

[7] LINGANE, J. J., *Ind. Eng. Chem., Anal. Ed.*, **17**, 640–642 (1945).

Deposition is from a tartrate solution with the potential at the cathode automatically[8] controlled to ±0.02 volt. Diehl[9] and Schleicher[10] deal with general applications.

A development in the use of controlled potentials for electrolytic separations, an outgrowth of work for the Manhattan District Project, is the use of a potential buffering solution, reported by Furman.[11] By controlling the total concentration of uranium, the deposition of chromium, molybdenum, man-
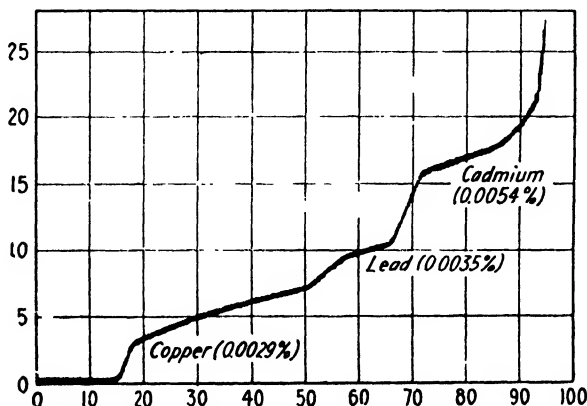

Fig. 13. Polarogram of copper, lead, and cadmium in a high-purity zinc-base die-cast alloy.

ganese, and other elements may be prevented when electrolysis with a mercury cathode is used for purposes of separation. An equilibrium between U(III) and U(IV) limits the decomposition potential at the cathode.

Most methods of electroanalysis depend on the electric current to precipitate an element or its compound from solution. The equivalence of the amount of an element precipitated with the amount of electricity expended (Faraday's law) provides another means for the quantitative estimation of an element and can be

[8] *Ibid.*, **17**, 332–333 (1945).

[9] DIEHL, H., "Electrochemical Analysis with Graded Cathode Potential Control," G. Frederick Smith Chemical Co., Columbus, Ohio, 1948.

[10] SCHLEICHER, A., "Elektroanalytische Schnellmethoden," 3d neubearbeitete Auflage von Fischer-Schleicher "Elektroanalytische Schnellmethoden," F. Enke, Stuttgart, 1947.

[11] FURMAN, N. H., *Chem. Eng. News*, **26**, 2490–2492 (1948); FURMAN, N. H., BRICKER, C. E., and McDUFFIE, B., *J. Wash. Acad. Sci.*, **38**, 159–166 (1948).

applied in a number of ways. Zakhar'evskiĭ in 1938[12] published one of the earliest applications of this principle when he determined lead and copper by depositing them from a solution and then measuring the current they generated as they redissolved. The same year Szebellédy,[13] using a platinum cathode and silver anode, was able to standardize, by electrolyzing at constant current and under conditions which produced a 100 per cent current yield, a number of relatively pure solutions with considerable precision. An interesting application of Faraday's law has been made by Lingane.[14] Employing cathode potential control, a mercury cathode, a silver anode, and a hydrogen-oxygen gas coulometer to measure current, he demonstrated the successive determination of copper and bismuth, which would have been difficult to accomplish by classical procedures in electroanalysis. Lead was also determined with satisfactory precision.

Ashley[15] reviewed electroanalytical studies by elements.

GENERAL REFERENCES

"Notes on Hydrogen Ion Measurements," Leeds & Northrup Company, Philadelphia, 1930.

CLARK, W. M., "Determination of Hydrogen Ions," The Williams & Wilkins Company, Baltimore, 1927.

KOLTHOFF, I. M., "Colorimetric and Potentiometric Determination of pH," John Wiley & Sons, Inc., New York, 1931.

BRITTON, H. T. S., "Hydrogen Ions," D. Van Nostrand Company, Inc., New York, 1932.

DOLE, M., "Experimental and Theoretical Electrochemistry," pp. 407–442, McGraw-Hill Book Company, Inc., New York, 1935.

LINGANE, J. J., *J. Am. Chem. Soc.*, **61**, 2099 (1939).

MACINNES, D. A., "The Principles of Electrochemistry," Reinhold Publishing Corporation, New York, 1939.

[12] ZAKHAR'EVSKIĬ, M. S., *Voprosy Pitaniya*, **7**, No. 4/5, 180–188 (1938); *Khim. Referat. Zhur.*, **2**, No. 4, 84 (1939).

[13] SZEBELLÉDY, S., and SOMAGYI, Z., *Z. anal. Chem.*, **112**, 313–323 (1938).

[14] LINGANE, J. J., *J. Am. Chem. Soc.*, **67**, 1916 (1945).

[15] ASHLEY, SAMUEL E. Q., *Anal. Chem.*, **21**, 70–75 (1949).

CHAPTER 7

ELECTROLYTIC REDUCTION AND OXIDATION

The electrolytic cell may be considered for the purpose of oxidation and reduction reactions as a source of the reductant hydrogen in its active or nascent form in surface layers of the cathode, or at the cathode interface, and as a source of nascent oxygen in similar locations related to the anode. If it be considered that the cell surface only is a source of reductant or oxidant, consideration should be given to the production of these at their highest efficiencies, after which the ordinary laws of chemical reactions should apply. The mass-action effects, concentrations, temperature of reaction, reaction velocities, diffusion, and equilibria between the initial and final products of the reaction, all apply to electrochemical reduction and oxidation in the same manner as do the same reactions carried on outside of the electrolytic cell. From the viewpoint that impurities should not be introduced into the system, it is desirable that the electrodes be of the unattackable type such as platinum and related metals, carbon, and metals of the nickel group for alkaline solutions; and the platinum metals and carbon in its various forms for acid solutions. Commercially, lead for sulfate and sulfuric acid solutions, graphite for chlorides, and nickel, iron, or steel for alkaline solutions are used.

From the electrochemical viewpoint, materials which are reduced may be considered cathodic depolarizers; those which are oxidized are anodic depolarizers. It follows that oxidation reactions may involve substances other than oxygen, such as chlorine for example. In general the anodes are selected with a high oxygen or halogen overvoltage, and cathodes are selected with a high hydrogen overvoltage. Substances which are easy to reduce may be acted on at the interface of cathodes with low hydrogen overvoltage; difficultly reducible materials may require much higher overvoltages reached as the result of the influence of either the cathode or the current density.

99

Electrolytic reduction may occur in the place of hydrogen evolution if the electrolyte contain readily reducible substances, when H^+ ions are discharged at the cathode. This reduction may proceed with high current density at a potential much less negative than that required for hydrogen evolution. The reduction process may result in changes of valence of ions such as that of ferric to ferrous ion or permanganate to manganate, or show its presence in the production of reduced compounds such as the formation of aniline from nitrobenzene. The cathodic reduction may be assumed to involve the discharge of H^+ ions to give atomic hydrogen dissolved in the cathode metal, followed by the reduction of the depolarizer or reducible substance by the atomic hydrogen. The velocity of depolarization is very important in electrolytic reduction. In this respect there is little difference between depolarizing electrolytes (*e.g.*, oxidizing agents) and nonelectrolytes (*e.g.*, nitrobenzene).

Each of the factors which affect hydrogen overvoltage will in turn affect electrolytic reduction. Increases in current density with corresponding increases in cathodic polarization will cause more H^+ ions to be discharged in unit time, with more rapid depletion of the layer of depolarizer around the electrode. There will then be a tendency for incompleteness of reduction, and a greater percentage of the current will be used in evolving hydrogen gas. Concentration of the depolarizer will affect depolarization and cathode potential. Similar effects will be caused by increases of temperature, agitation, or other means to cause the depolarizer to diffuse more effectively.

The theories of electrolytic reduction and oxidation have been discussed extensively and in the classical manner by Foerster.[1] The utility and value of the c.d.-cathode potential curves were pointed out by Haber.[2]

In the reaction between a depolarizer and hydrogen, the catalytic effect of the cathode will vary with the cathode material. Hence a reduction process may occur at one cathode with a much less negative cathode potential than is possible at another. Conversely, at a given cathode potential a wide variation of cur-

---

[1] FOERSTER, F., "Elektrochemie wässeriger Lösungen," pp. 570–599, J. A. Barth, Leipzig, 1923.

[2] HABER, F., *Z. physik. Chem.*, **32**, 193 (1900); *Z. angew. Chem.*, 1900, 433; *Z. Elektrochem.*, **7**, 304 (1900).

rent density is possible. In acid solution the reduction of nitro-benzene to aniline takes place more readily at a zinc cathode than at platinum,[3] but in an alkaline solution iron, zinc, tin, and lead are far less effective than either platinum or copper. It has been found that the use of an iron cathode will permit the electrolytic reduction of chlorates ordinarily irreducible.[4] In like manner the reactions are affected by the surface condition of the metal. For instance, the reduction of nitrates will yield ammonia at a smooth copper cathode but nitrites at a spongy
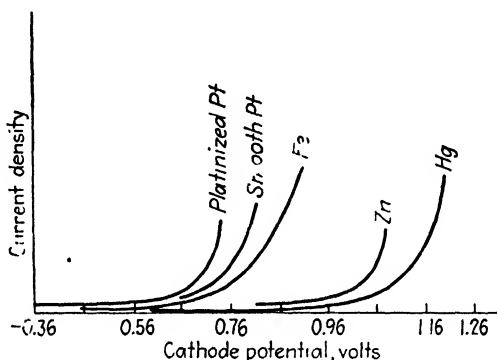

Fig. 14. Cathodic reduction of N KNO$_3$ with $N/100$ KOH. (*Müller.*)

electrode.[5] Figure 14 shows the current-cathode potential curves produced by the use of various cathode materials in the reduction of a slightly alkaline N KNO$_3$ solution.[6] These curves indicate the wide difference in potential required as the result of variation in the catalytic action of cathode metals. Indigo is reduced only at zinc cathodes to indigo white.[7]

The type of cathode metal used may further affect electrolytic reduction by increasing the polarization required for H$^+$ ion discharge. From Fig. 15, in which AB is the current-cathode potential curve for reversible hydrogen discharge and DE the curve for the reduction process, it is seen that, if the given cathode permit reversible H$^+$ ion discharge, the total current will be

[3] ELBS, K., *Z. Elektrochem.*, **2**, 473 (1895).

[4] HENDRIXSON, W. S., *Am. Chem. J.*, **32**, 242 (1904).

[5] MUELLER, E., and WEBER, J., *Z. Elektrochem.*, **9**, 955 (1903).

[6] MÜLLER, E., *Z. anorg. Chem.*, **26**, 1 (1901).

[7] BINZ, A., and HAGENBACH, A., *Z. Elektrochem.*, **5**, 103 (1898); **6**, 261 (1899).

used in hydrogen evolution. The curves are such as those developed by Müller and his coworkers[8] and Russ.[9] However, should the hydrogen overvoltage be sufficiently great, the curve AB will
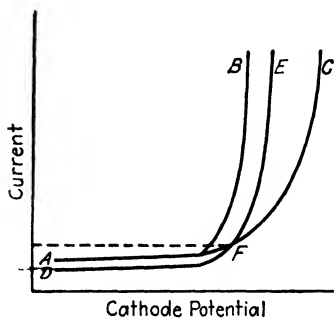

Cathode Potential

Fig. 15.

assume the form AC. Reduction will then begin at a current density above that corresponding to F, proceeding along with hydrogen evolution. Similarly in Fig. 16 the curve F is shown to cut the reversible H^+ ion discharge curve G. As the hydrogen overvoltage increases, the hydrogen curve will take the form ACH. Yields of reduced material will approach 100 per cent even at high current density.

Through the use of such cathodes, reductions requiring very large cathodic polarization are effected. Such substances as pyridine and various alkaloids of the uric acid group, all reducible only with difficulty, have been extensively studied.

Catalysts of the "carrier" type in the electrolyte at times have an important place in electrolytic oxidation and reduction. These are commonly metals which have multiple valence ions such as titanium, vanadium, cerium, manganese, and uranium salts. The carriers will be oxidized at the anode and reduced at the cathode and may thus be an intermediate reactor.
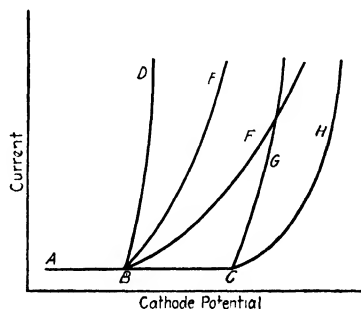

Cathode Potential

Fig. 16. $ABCG$ for reversible H^+ ion discharge. ABD shows effect of rapidly acting depolarizer, ABE effect of moderately active depolarizer, ABF less active depolarizer. $ABCH$ shows effect of hydrogen overvoltage increase.

In contrast to chemical methods, electrolytic oxidation and reduction may be a stepwise process controlled by variation of temperature, cathode potential, electrode material, overvoltage, and concentration of products. None of the reacting agents, as

[8] Müller, E., *Z. anorg. Chem.*, **26**, 1 (1901).

[9] Russ, F., *Z. physik. Chem.*, **44**, 641 (1900).

employed in ordinary chemical methods, appear as impurities in the final product. The aromatic nitrogen-containing organic compounds have been extensively studied, particularly by Haber[10] and Elbs[11] who with other workers showed that the nitro compounds of the type RNO_2, where R would be an organic radical, could be reduced to the nitroso product RNO, to the beta aryl hydroxylamine RNHOH, to the azoxy product

RN——NR, to the material containing an azo group RN═NR,
$\diagdown\diagup$
O

which in turn is reduced to the hydrazo form RNH—NHR, or to the idene type as H_2NR—RNH_2, and finally to the amine RNH_2.

Electrolytic Oxidation. Oxidizable substances may act toward the OH⁻ ion discharge in a manner similar to the depolarization of a H⁺ ion discharge by a reducible substance. The process is "electrolytic oxidation." It may involve valence-change oxidation such as the conversion of ferrous to ferric ion, or the manganate to the permanganate ion; polymerization of ions such as the conversion of sulfates to persulfates in which sulfur is oxidized; or reactions in which the oxygen content of a substance increases as in the conversion of ammonia to nitrite, or the hydrogen content diminishes as in the conversion of formic acid to carbon dioxide. Everything that has been said about hydrogen depolarization applies to depolarization of oxygen. The reversible potentials at which many oxidations take place are generally much nearer to the potential required for free oxygen evolution than are the corresponding values for hydrogen. Oxygen evolution potentials in electrolytic oxidation may be reached at relatively low current density. The yield of oxidized product then falls below 100 per cent. The anodic polarization may then slowly increase as the result of rising oxygen overvoltage. Such high oxidizing potentials may be reached that organic depolarizers may be oxidized more than desired. Low yields of the products may result.

The variables of current density, temperature, concentration, electrodes, and other factors have effects similar to those pro-

[10] HABER, F., *Z. Elektrochem.*, **4**, 506, 577 (1898); *Z. physik. Chem.*, **32**, 271 (1900); *Z. angew. Chem.*, 1900, 433.
[11] ELBS, K., *Z. Elektrochem.*, **7**, 133 (1900).

duced in cathodic reduction. The OH^- ion concentration determines the potential at which oxygen evolution can begin. This is higher in acid solution. Oxidation of difficultly oxidizable substances is best carried out in acid electrolytes. The OH^- ion concentration may actually alter the nature of the substance being oxidized. If it be an acid and the anolyte made alkaline, the anion of the acid will be submitted to oxidation. If, however, the anolyte be acidified by a strong mineral acid, the depolarizing acid if not a strong one will be present largely as undissociated molecules. The results of oxidizing anion and undissociated acid can sometimes be very different.

The importance of the nature of the electrode material can be seen from the table of oxygen overvoltages. The electrode may be of use because of its oxygen overvoltage on the one hand, or on the other because of its catalytic influence on the reaction between oxygen and depolarizer. Materials difficult to oxidize necessitate the use of electrodes with high oxygen overvoltage and a high current density. An example of the catalytic effect of the anode may be seen in the oxidation of iodic (HIO_3) to periodic acid (HIO_4). Müller and Friedberger[12] have shown that a current efficiency of 100 per cent may be obtained at an anode of PbO_2 and only 1 per cent at a smooth platinum anode. Similar effects of the PbO_2 anode are noted in the oxidation of Cr^{+++} to CrO_4^{--}.

So-called "oxygen carriers," such as cerous sulfate $[Ce_2(SO_4)_3]$, as additions to the electrolyte may have important effects on the efficiency of electrolytic oxidation. The cerium salt can be rapidly oxidized anodically to the ceric form which oxidizes many organic substances. In copper refining the anodic oxidation and cathodic reduction of iron salts have a very important effect on the efficiency of refining, markedly reducing the current and energy efficiency when these are considered from the viewpoint of copper deposition.

Organic Electrochemistry. An extensive literature has been built up on organic electrochemistry,[13] but only very few processes

[12] MÜLLER, E., and FRIEDBERGER, O., *Ber.*, **35**, 2655 (1902); MÜLLER, E., *Z. Elektrochem.*, **10**, 61 (1904).

[13] BROCKMAN, C. J., "Electro-organic Chemistry," John Wiley & Sons, Inc., New York, 1926.

in this field have found commercial application. In electrolytic oxidation or reduction of organic compounds, the material to be oxidized or reduced is usually the depolarizer. Organic compounds are too poor conductors to be used without an added electrolyte. It is difficult to regulate the electrode potential for any one reaction so that all the oxygen at the anode or hydrogen at the cathode is absorbed by the depolarizer. The amount of oxidation or reduction is a function of the nature of the depolarizer, the current density at the anode or cathode (because of its influence on the rate of gas evolution), the concentration of the depolarizer, its diffusion, mechanical effects such as stirring, catalytic influence of added compounds, temperature, the nature of the anode material, and the solvent.

The literature on electroorganic chemistry is in a very confused state. Swann concludes that "electroorganic methods compare favorably with purely chemical methods for syntheses involving coupling, oxidation, halogenation, and reduction."[14] Swann tabulated the organic preparations which give yields equal or superior to those obtained by purely chemical methods. His original papers should be consulted. A few examples of electrolytic oxidation or reduction of organic compounds will be discussed.

The usefulness of the electrolytic method for the preparation of organic materials is limited by the solubility of the depolarizer. McKee and his coworkers[15] found that organic depolarizers will dissolve to an appreciable extent in the concentrated solutions of alkali metal aromatic sulfonates, and this extended the possible scope of electrolytic reduction of organic compounds. The industrial possibilities of electroorganic reduction are pointed out by Swann.[16]

A suspension of anthracene in H_2SO_4 may be anodically oxidized at a platinum anode to anthraquinone. In the presence of carriers such as cerium, vanadium, or chromium salts, the efficiency of the operation is markedly improved. The cerium salt is anodically oxidized and in turn oxidizes the anthracene.

[14] SWANN, S., *Trans. Electrochem. Soc.*, **69**, 287 (1936).

[15] McKEE, R. H., and BROCKMAN, C. J., *Trans. Electrochem. Soc.*, **62**, 203 (1932); McKEE, R. H., and GERASTOPOLOU, B. G., *ibid.*, **68**, 329 (1935).

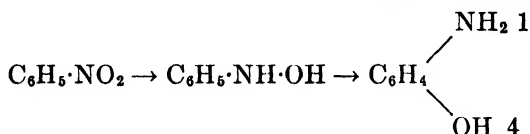[16] SWANN, S., *Ind. Eng. Chem.*, **29**, 1339 (1937).

Chromic acid, when employed, is commonly regenerated externally. The commercial details of the process are given in Table 13.

TABLE 13.   ORGANIC OXIDATION PRODUCTS

Raw material	Anthracene	Nitrobenzene
Product	Anthraquinone	Para-aminophenol
Anolyte[1]	Anthracene suspended in 20 per cent H_2SO_4	81–82 per cent H_2SO_4
Catholyte[1]	Same as anolyte	Nitrobenzene in 91 per cent H_2SO_4
Catalyst or carrier	2 per cent $Ce(SO_4)_2$	
Temperature, °C	70–100	30–40
Anode c.d., amp/sq ft	46–47	
Cathode c.d., amp/sq ft	. . . . .	27.9–37
Voltage	2.8–3.5	8
Current efficiency, per cent	100	25
Tank	Lead-lined steel	
Diaphragm	None	Unglazed porcelain
Diaphragm, voltage drop	.	4
Material yield, per cent		40–50
Energy, kwhr/lb	.	9.1–11.4

[1] That portion of the electrolyte surrounding the anode is anolyte; around the cathode, catholyte.

Para-aminophenol was made in the United States on a fairly large scale during the First World War by Thatcher's method, by the reduction of nitrobenzene in concentrated H_2SO_4 solution at platinum cathodes.[17]   The actual reduction product is phenyl-hydroxylamine, which, as the result of intramolecular change, is converted into para-aminophenol according to the reaction:

$$C_6H_5 \cdot NO_2 \rightarrow C_6H_5 \cdot NH \cdot OH \rightarrow C_6H_4 \underset{\searrow}{\overset{\nearrow}{}} \begin{matrix} NH_2 \ 1 \\ OH \ 4 \end{matrix}$$

The details of the commercial practice are given in Table 13.

The hexahydric alcohols sorbitol and mannitol, $C_6H_6(OH)_6$, are produced by electrolytic reduction of dextrose or cerelose. The manufacturing method is given in the flow sheet in Fig. 17 and the operating details in Table 14.   The practice follows

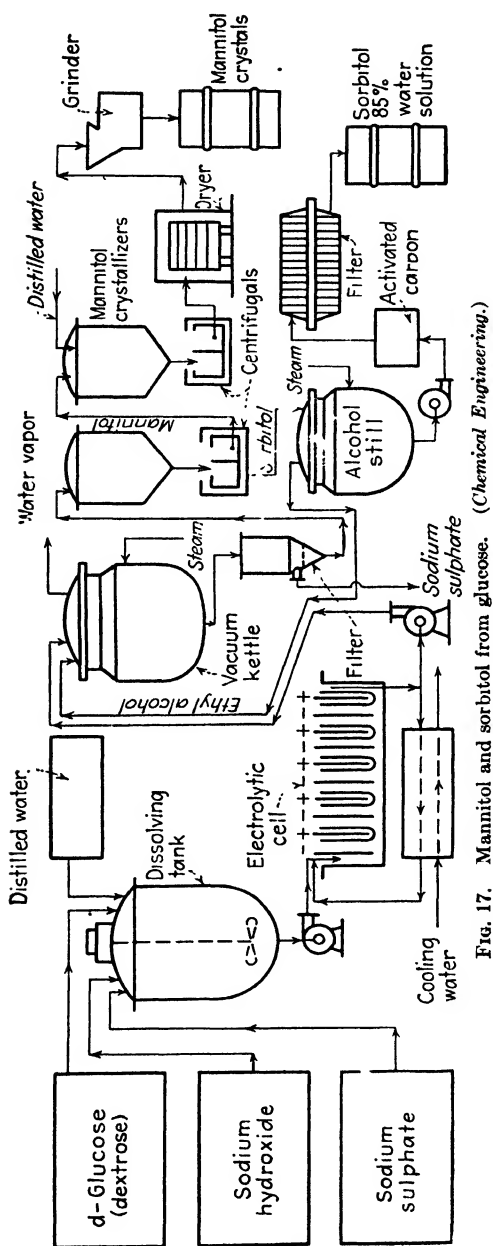[17] McDANIEL, A. S., SCHNEIDER, L., and BALLARD, A., *Trans. Am. Electrochem. Soc.*, **39**, 441 (1921).

Fig. 17. Mannitol and sorbitol from glucose. (*Chemical Engineering.*)

that outlined in the Creighton patents,[18] while Fig. 18 shows a typical cell room.

The electrolyic action in the cell is simple.   The water in the two electrolyte solutions is decomposed by the current to liberate at the cathode nascent hydrogen, which reduces the glucose to sorbitol and mannitol, and at the anode nascent oxygen, which

FIG. 18.   Cell room for electrolytic reduction of glucose to sorbitol.   (*Atlas Powder Co.*)

forms lead peroxide.   This latter compound is recovered as a by-product of the process.

The process does not yet lend itself to continuous operation; so all equipment and materials handling facilities are designed for batch work.   Purified glucose, the chief raw material, is dissolved in distilled water to give a concentrated solution.   The glucose solution is made alkaline by sodium hydroxide, and sodium sulfate is added to raise its electrical conductivity.

The solution is pumped to the electrolytic cells.   Each cell consists of an open-top rectangular tank about 13 ft long, 6 ft

[18] CREIGHTON, H. J., U.S. Patents 1,612,361 (1926); 1,653,004 (1927); 1,712,951 (1929); 1,712,952 (1929); 1,990,582 (1935).

wide, and 3 ft deep, in which are suspended, alternately, 35 anodes and 36 cathodes, each of which is in the form of a rectangular plate with dimensions corresponding to the width and depth of the tank.   The anode is of pure lead, while the cathode is a lead-mercury amalgam, the lead serving merely as a holder for the mercury electrode.   Completely surrounding each anode is a diaphragm of unglazed porcelain which encloses the dilute

TABLE 14.   SORBITOL AND MANNITOL

Raw material...	Purified glucose. NaOH and Na_2SO_4 are added to alkalize and to bring electrical conductivity up to requirements
Anolyte...............	Dilute H_2SO_4 solution
Catholyte.	Glucose solution
Temperature....... . .	Room
Current	D.c supplied by 4 motor-generator sets, 5,000 amp at 20 volts
Anode material. .	Pure lead
Cathode material.	Pb-Hg amalgam
Diaphragm material . .	Unglazed porcelain
Cells:	
Material... .. .	Glass- or rubber-lined equipment
Number . .	12
Size. ..	$13 \times 6 \times 3$ ft
Number anodes, cathodes	35, 36
Baffles.	Between every group of 6 pairs of electrode plates

H_2SO_4 anolyte and keeps it apart from the glucose solution which serves as the catholyte.

Electrolytic Reduction and Oxidation Applications. Relatively little application has been made of electrolytic reduction processes.   At one time such a method was applied to the reduction of galena or PbS ores in a H_2SO_4 solution.   The operation was carried on for a while at Niagara Falls.[19]   The manufacture of chromous salts by electrolytic reduction has been investigated and methods worked out.[20]   Similar suggestions have been made in connection with sodium hyposulfite, commonly called "hydrosulfite" ($Na_2S_2O_4$), by the electrolytic reduction of $NaHSO_4$ or of sulfites.[21]

[19] SALOM, P., *Trans. Am. Electrochem. Soc.*, **1**, 87 (1902); **4**, 101 (1903).

[20] BOEHRINGER, C. F., and SÖHNE, German Patent 115,463 (1899).

[21] JELLINEK, K., *Z. Elektrochem.*, **17**, 245 (1911); Badische Anilin und Sodafabrik, German Patent **276,058** (1912).

Persulfates. The manufacture of persulfates, such as ammonium persulfate, is complicated by many factors. Two peracids of sulfur exist; *viz.*, the permonosulfuric acid or Caro's (H_2SO_5) and perdisulfuric acid commonly called persulfuric acid ($H_2S_2O_8$). The ammonium persulfate of commerce is the salt of the latter acid, having the formula $(NH_4)_2S_2O_8$.

When an aqueous solution of fairly concentrated H_2SO_4 is electrolyzed between platinum electrodes using a high current density at the anode, $H_2S_2O_8$ is first formed by the discharge of the HSO_4^- ions, in accordance with the equation

$$2HSO_4^- + 2\oplus = H_2S_2O_8$$
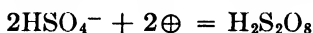
In the presence of H_2SO_4, however, this acid is not very stable and changes more or less quickly, depending upon the concentration of the H_2SO_4, into H_2SO_5, as shown by the equation

$$H_2S_2O_8 + H_2O = H_2SO_5 + H_2SO_4$$
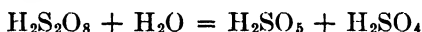
The H_2SO_5 can then undergo further decomposition with the production of H_2O_2

$$H_2SO_5 + H_2O = H_2SO_4 + H_2O_2$$
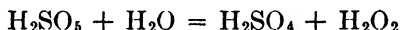
The two acids are readily distinguished from H_2O_2 by the fact that they do not decolorize permanganate or give rise to the characteristic colorations produced by H_2O_2 with titanium salts, or with chromic acid; but it is more difficult to differentiate them from each other in aqueous solution.

Sulfuric acid of a density of 1.39 to 1.4 gives a maximum yield of $H_2S_2O_8$. The influence of anode current density is shown in Fig. 19, obtained with an acid density of 1.38 at temperatures of 8 to 10°C, the duration of electrolysis being 50 min.

The temperature at which the electrolysis is done is very important. A rise of temperature diminishes the yield which becomes practically zero at 60°, the $H_2S_2O_8$ decomposing as fast as it is formed. Cooling the anode has a favorable effect as far as increasing the current efficiency is concerned. The presence of small quantities of many metallic sulfates, especially those of ammonium, potassium, nickel, and aluminum, favors the formation of $H_2S_2O_8$. The addition of a drop of concentrated HCl increases the yield from 46 to 69 per cent.

In the preparation of $(NH_4)_2S_2O_8$, the electrolyte is either a

saturated solution of purified $(NH_4)_2SO_4$ or else an almost saturated solution of this salt made acid with H_2SO_4. The electrode materials are platinum anodes in the shape of either sheet, gauze, or wire, alone or held in a frame of a metal such as zinc; or sometimes tantalum plated or coated with platinum, often in the form of flattened wire, while cathodes are generally lead, either in the form of the tank lining or coils of pipe, or cast sections of lead which may be water-cooled, or in some cases aluminum. Cur-
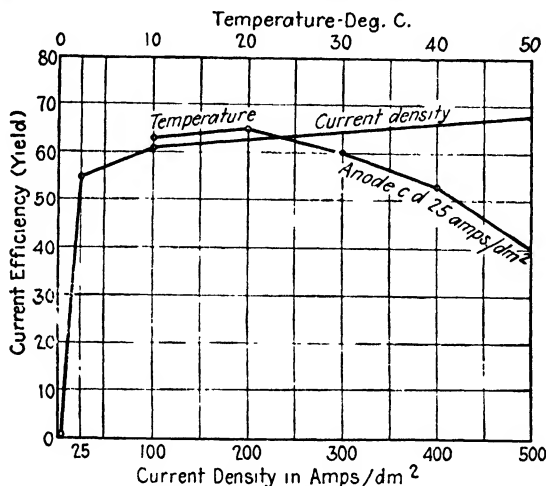

FIG. 19. Anode current density and temperature effects in persulfate formation.

rent densities are of the order of 280 to 465 amp per sq ft (30 to 50 amp per dm²), with emf of 6 to 7 volts. It is general practice to add 0.2 per cent of $K_2Cr_2O_7$ or K_2CrO_4 to the electrolyte to reduce cathodic reduction of the persulfate formed. Commercial cells vary considerably in size, from units as small as 250-amp capacity to as large as 1,500-amp. In larger units anode arrangements and mechanical difficulties in securing proper placement and rigidity of anode surface cause trouble. The tanks are of either cement or wood with lead linings or of chemical stoneware. Cooling of the electrolyte is done either in a system in which the electrolyte is continuously circulating and the $(NH_4)_2S_2O_8$ being produced is continuously removed (the liquor being cooled outside the cells in holding tanks) or the liquor is cooled by the use of lead cooling coils which are made part of the cathode surface in the tank.

It has been found practical in commercial operation to allow the temperatures to rise as high as 30°C without appreciable lowering of current efficiency. Temperatures higher than this markedly decrease the current efficiency, and lower temperatures increase it. Ammonium persulfate begins to decompose at 40°C. The effect of temperature on the yield is shown in Fig. 19.

Large cells are roughly 8 ft 6 in. long, 3 ft 2 in. to 4 ft 3 in. high, and 3 ft 2 in. to 4 ft 10 in. wide (2.6 m long, 1 to 1.3 m high, 1 to 1.5 m wide), operating at 1,500 amp. The energy requirements in medium-size cells—*i.e.*, 500- to 750-amp capacity —are of the order of 2.1 to 2.5 kwhr per kg $(NH_4)_2S_2O_8$ produced (0.95 to 1.1 kwhr per lb), with poorer operation and continuous running under average control tending toward the higher figure rather than the lower one.

Perborates. The electrolytic cells for the manufacture of sodium perborate have not been developed to so large a size as those for ammonium persulfate and potassium perchlorate. The perborates differ from the persulfates in that they are most readily obtained from the borates by direct interaction with H_2O_2 or with the peroxides of the alkali metals, and not by the electrolysis of solutions of the borates. The best known salts are derivatives of metaboric acid, $HO \cdot B\!:\!O$. Since they are very readily hydrolyzed in aqueous solution, with the formation of H_2O_2, their constitution may be represented as $MO \cdot OB\!:\!O$, where M is a univalent metal.

Sodium perborate, $NaBO_3 \cdot 4H_2O$, is readily obtained when a saturated solution of borax containing an equivalent quantity of NaOH is treated with an excess of H_2O_2 (double the amount necessary for the production of $NaBO_3$). After some time large, transparent, prismatic crystals of the salt separate.

$$Na_2B_4O_7 + 2NaOH + 4H_2O_2 = 4NaBO_3 + 5H_2O$$

Anodes and anode arrangements as well as anode materials are the same as for persulfates. Current densities are lower than in the case of persulfates, being of the order of 140 to 186 amp per sq ft (15 to 20 amp per dm²). Low current concentrations are necessary, which means that there is a relatively large volume of solution. Cathodes are either tin tubes, which are cooled, or tin plates, although in some cases zinc and aluminum have been used. Cathode current densities are of the order

of 46 to 93 amp per sq ft (5 to 10 amp per dm^2).   In some cases lead has been successfully employed, either in sheet form or in the tube form, as anode.   In Europe magnetite anodes have been used.   They may last 2 to 3 years but are useful only for low current density of the order of 18 to 28 amp per sq ft (2 to 3 amp per dm^2).   They are difficult to handle, fairly fragile, and necessitate close control.   The electrolyte cells or tanks have been constructed of wood such as cypress which has been previously treated with waxes, creosotic materials, or other impregnating agents to increase their life.   Voltages across the cells are 7 to 7.5. the power consumption per kilogram of $NaBO_3$ being of the order of 6 to 6.5 kwhr (2.7 to 3 kwhr per lb).   A common electrolyte consists of 40 g $Na_2B_4O_7 \cdot 10H_2O$ (borax) per liter, 140 g Na_2CO_3 per liter, 2 g $Na_2Cr_2O_7$, which amount is at times decreased and at other times slightly increased, depending upon losses due to cathodic reduction, and, depending upon the particular plant practice, small additions of Na_2SiO_3 or colloidal substances like glue and turkey red oil may be added to the electrolyte.

Liquors are circulated through the cells, continuously filtering out the crystalline $NaBO_3$ which precipitates in the cells.   In the simplest type of arrangement, liquor is fed from a refrigerating tank to the cells, passing through them to the outside, and on to a filtering surface of either asbestos sheet, in some cases fused alumina, or filtros, the liquors then passing to holding tanks where their composition is adjusted by the addition of borax, Na_2CO_3, and sometimes $NaHCO_3$ because of CO_2 losses. From the holding tank the liquor passes through the refrigeration tank for another cycle of circulation.   In the simplest form of circulation system, anolyte and catholyte may be kept separate by the use of a diaphragm in the cell, and separate outlets for anolyte and catholyte are provided.   Modern cells are not provided with diaphragms and both sides of the anode surface are effectively used.
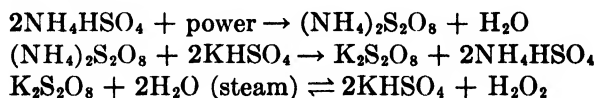
Hydrogen Peroxide.   Hydrogen peroxide is produced by the distillation of per compounds such as persulfuric acid produced by electrolysis and distilled *in vacuo* with the formation of H_2O_2 and H_2SO_4 which is reelectrolyzed.   Ammonium persulfate may be produced electrolytically, decomposed with potassium bisulfate or H_2SO_4 to give H_2O_2.   In a third method ammonium

persulfate is prepared electrolytically and decomposed under vacuum with the production of ammonium bisulfate solution, which is returned to the electrolytic cells. Skirrow and Stein[22] studied the distillation of recrystallized electrolytically produced potassium persulfate with H_2SO_4 for the production of H_2O_2.

TABLE 15. HYDROGEN PEROXIDE PRODUCTION BY AMMONIUM PERSULFATE

Cell:

Length × width × depth.	95 × 70 × 95 cm
	(37.4″ × 27.56″ × 37.4″)
Materials...	Porcelain
Cell voltage....	5 7
Cell amperage . . .	5,400
Current efficiency, %.	85
Anodes:	
Material.	Platinum, 14 per block
Number per cell	6 blocks
Diaphragm......	Blue asbestos rope
Cathodes:	
Material...	Graphite
Number per cell.....	30
Shape	Rods
Power per kg (100% ≂), kwhr. ..	17 5
Steam, kg	28
Water, m³... .	3

Electrolysis of ammonium acid sulfate in sulfuric acid solution yields ammonium persulfate which by metathesis with potassium bisulfate produces relatively insoluble potassium persulfate. The potassium persulfate is hydrolyzed with live steam, and the resultant vapors are rectified under reduced pressure and condensed to yield an aqueous solution of hydrogen peroxide. The reactions are as follows:

$$2NH_4HSO_4 + \text{power} \rightarrow (NH_4)_2S_2O_8 + H_2O$$
$$(NH_4)_2S_2O_8 + 2KHSO_4 \rightarrow K_2S_2O_8 + 2NH_4HSO_4$$
$$K_2S_2O_8 + 2H_2O \text{ (steam)} \rightleftharpoons 2KHSO_4 + H_2O_2$$

Operating conditions of a German plant are given in Table 15. Forty-four porcelain electrolytic cells about 95 cm long, 70 cm wide, and 95 cm deep were used, generally in series with 230 volts. Four of the cells were usually out of operation for maintenance, making the voltage of each cell about 5.7 volts; 5,400 amp were

[22] SKIRROW, F. W., and STEIN, E. R., *Trans. Am. Electrochem. Soc.*, **38**, 209 (1920).

utilized at a current efficiency of 85 per cent. Ammonium thiocyanate (0.1 g per liter) was placed in the electrolyte to increase the oxidation tension or overvoltage. There were six blocks of electrodes and glass cooling tubes in each cell. Each block contained 14 platinum wire anodes supported by rubber-covered aluminum tubing and 30 graphite rod cathodes wound with blue asbestos rope to serve as a diaphragm. The electrodes were so arranged that each anode was surrounded by four cathodes with an effective minimum distance of about 5 mm. A forced air current above the cells maintained the hydrogen gas concentration below 5 per cent.

A filter removed graphite, asbestos, etc., from the electrolyzed solution, which was cooled by a vacuum cooler in which about 2 per cent of the water was removed and the temperature decreased from 30 to about 26°C. The product then passed to a converter where the second reaction above was carried out. The potassium persulfate was separated by a centrifuge before steam distilling in a porcelain retort. The resultant vapors were rectified at a pressure of about 38 mm mercury to produce a 35 per cent solution of hydrogen peroxide which served as stock for the preparation of concentrated hydrogen peroxide.

Although the sulfuric acid recovered from the solution contained about 10 mg per liter of such metals as iron and aluminum, the iron content was reduced to less than 5 mg per liter before reuse by precipitating prussian blue from the solution. This step also removed the platinum content.
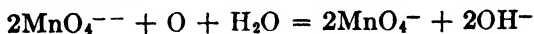
Permanganates. Manganates are made by heating KOH and finely ground MnO_2 in air according to the reaction

$$MnO_2 + 2KOH + O = K_2MnO_4 + H_2O$$

The reaction does not go to completion, and there is always some unchanged KOH. The manganate is dissolved, filtered, and oxidized to permanganate either by means of chlorine and H_2SO_4, or CO_2, or electrolytically according to the reactions

$$2K_2MnO_4 + Cl_2 = 2KCl + 2KMnO_4$$
$$3K_2MnO_4 + 2CO_2 = 2KMnO_4 + 2K_2CO_3 + MnO_2$$

or by anodic oxidation

$$2MnO_4^{--} + O + H_2O = 2MnO_4^- + 2OH^-$$

The electrolytic production of permanganate from manganates was studied by Askenasy,[23] whose results are summarized in Table 16, column 1.

Lorenz[24] has shown that permanganates may be made by the anodic oxidation of manganese or ferromanganese anodes in a NaOH or KOH electrolyte. The iron is oxidized and with part of the manganese forms anode mud. Oxide scales which insulate the anode are formed in KOH solutions, but with K_2CO_3 this does not happen if the temperature be maintained at 40°C or below. When 75 per cent Mn ferroalloys are used, about 60 per cent of the manganese is converted into permanganate. The yield of $KMnO_4$ decreases with decrease in manganese content of the anodes, and under 40 per cent Mn there is no yield of $KMnO_4$. Cobalt is the only harmful impurity, a 2 per cent content in the anode completely preventing the formation of permanganate. Wilson, Horsch, and Youtz[25] studied the use of ferromanganese in a K_2CO_3 electrolyte. Their results are tabulated in Table 16, column 2. Desmet[26] gives typical figures for the operation of commercial plants producing permanganates from manganates in column 3.

Silicomanganese has been proposed as a substitute for ferromanganese in that this material as an anode disintegrates more readily and is less liable to become coated with an insulating layer.[27]

Ferricyanides. Electrolytic oxidation has to some extent displaced chemical oxidation of ferrocyanide to ferricyanide by chlorine according to the reaction

$$2K_4Fe(CN)_6 + Cl_2 = 2K_3Fe(CN)_6 + 2KCl$$
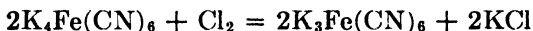
because of the difficulty in separating the ferricyanide and KCl. Electrolytic oxidation is according to the reaction

$$2K_4Fe(CN)_6 + O + H_2O = 2K_3Fe(CN)_6 + 2KOH$$
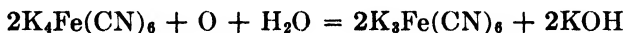
[23] Askenasy, P., *Tech. Electrochem.*, **2**, 72 (1916).

[24] Lorenz, R., *Z. anorg. Chem.*, **12**, 393 (1896).

[25] Wilson, R. E., Horsch, W. G., and Youtz, M. A., *J. Ind. Eng. Chem.*, **13**, 763 (1921).

[26] Desmet, R., *Ind. chim. belge*, **8** (2), 169 (1937).

[27] French Patent 675,477.

TABLE 16. INORGANIC OXIDATION PRODUCTS

	(1)	(2)	(3)	(4)	(5)
Raw material	K_2MnO_4	Ferromanganese (75% Mn)	K_2MnO_4	$K_4Fe(CN)_6$	$K_4Fe(CN)_6$
Product	$KMnO_4$	$KMnO_4$	$KMnO_4$	$K_4Fe(CN)_6$	$K_4Fe(CN)_6$
Anolyte	Solution of K_2MnO_4	14% K_2CO_3 solution	Solution of K_2MnO_4	Saturated $K_4Fe(CN)_6$ solution	180 g/l $K_4Fe(CN)_6$
Catholyte	Same as anolyte	75 Mn ferromanganese	Same as anolyte	Dilute KOH	5% KOH
Anode	Sheet iron	Sheet iron	Iron	Ni, Pt, or Cu	Graphite
Cathode	Iron rods		Iron	Iron	Iron
Anode c.d., amp/sq ft	84	56-84	93	4 75-18 6	9.3
Cathode c.d., amp/sq ft	840		790		
Diaphragm material	None	Porous porcelain		Unglazed porcelain	
Diaphragm voltage drop	.	High	.	High	.
Temperature, °C	60	20	60	25-50	18
Cell voltage	3	6 5	2 8		3
Current efficiency, %	70	30-35	55	80-90	96
Tank material	Steel	Steel			
Energy, kwhr/lb	.	10-11	0 37-0 41		
Lb per kwhr	3 1				

(1) Tech. Electrochem., **2**, 72 (1918).
(2) J. Ind. Eng. Chem., **13**, 763 (1921).
(3) Ind. chm. belge, **8**, (2) 169 (1937).
(4) Z. Elektrochem., **20**, 334 (1914).
(5) J. Phys. Chem., **24**, 230 (1920).

and takes place with a high current efficiency when a diaphragm is used to prevent cathodic reduction of the ferricyanide. Film-forming additions such as chromates are not useful in this respect. Grube[28] used a saturated solution of $K_4Fe(CN)_6$ as an anolyte and either a half-saturated solution or dilute KOH as catholyte, the two being separated by an unglazed porcelain diaphragm. Grube's results are summarized in column 4 of the same table. The anode material had little effect on the current efficiency or the point at which oxygen evolution started. Brown, Henke, and Miller,[29] using graphite anodes and diaphragms, obtained a 96 per cent current efficiency, with the production of pure ferricyanide. Their results are tabulated in column 5.

Regeneration of Chromic Acid. Chromic acid is used as an oxidizing agent in the preparation of many organic compounds, being reduced to chromium salts which in some cases are thrown away and in others regenerated by electrolytic oxidation. In the latter case, a typical solution containing the equivalent of 100 g per liter H_2CrO_4 as sulfate and 350 g per liter of H_2SO_4 is electrolyzed with lead electrodes in a lead-lined tank divided by a diaphragm. The anodes become covered with PbO_2, and H_2CrO_4 is formed in the anolyte according to the equations

$$2Cr^{3+} + 3O + 3H_2O = 2Cr^{6+} + 6OH^-$$
$$2Cr^{6+} + 16OH^- = 2CrO_4^{--} + 8H_2O$$
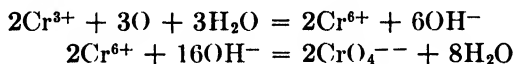
In spite of the fact that the voltage at a given current density is higher with a platinum than with a lead electrode in a H_2CrO_4-H_2SO_4 solution, the reaction does not take place on smooth platinum anodes. In this case, however, the presence of a small amount of lead salt in solution catalyzes the reaction. The current efficiency is 70 to 90 per cent at 3.5 volts per cell. Hydrogen is liberated at the cathode and H_2SO_4 concentrates at the anode. The anolyte solution is used directly for oxidation. It is then circulated through the cathode compartment where the concentration of H_2SO_4 is reduced, after which it passes to the anode for oxidation and the cycle is repeated. A large amount of

[28] GRUBE, G., *Z. Elektrochem.*, **20**, 334 (1914).
[29] BROWN, O. W., HENKE, C. O., and MILLER, I. L., *J. Phys. Chem.*, **24**, 230 (1920).

experimental work has been done on the electrolytic regeneration of H_2CrO_4.[30]

Thompson[31] has suggested that a large amount of SO_2 produced in roasting sulfide ores might be used to depolarize insoluble anodes in electrowinning operations. The SO_2 is oxidized to H_2SO_4 and the cell voltage reduced.

Electrolytic White Lead. The Sperry process for the electrolytic production of white lead employs a bifluid cell whose lead anode and iron cathode are separated by a linen diaphragm. Solutions of sodium acetate containing sodium carbonate form the electrolytes. The anolyte contains the exact amount of carbonate necessary to precipitate the white lead. This concentration is maintained by feed from the catholyte in which there is a relatively large amount of carbonate. As the lead dissolving from the anode surface reprecipitates as basic carbonate in the anolyte, the passage through the partition of CO_3^{--} ions from the catholyte counteracts the carbonate loss, maintaining a constant concentration in the anode compartment. The process continues in this manner, producing a compound of uniform composition and brilliant white color. Both electrolytes are circulated rapidly, the composition of the anolyte remaining unchanged. As the catholyte passes through the cell, it gives up the required amount of CO_3^{--} ions to the anolyte, then flows through a CO_2 absorption tower to be brought back to its original composition. White lead, suspended in the anolyte, is continuously removed by settling and filtration, the clear electrolyte returning to the cell. The anode is ordinarily of lead from which any silver content has been removed. Its degree of purity has no bearing upon the purity of the resultant white lead, since any metals present other than lead do not dissolve with the latter but form a slime on the anode surface. This is cleaned off periodically, and the collected mass is treated for the recovery of the various metallic constituents.

The electrolytic cells used at the plant of the Anaconda Lead

[30] LeBlanc, M., *Z. Elektrochem.*, **7**, 290 (1901); Askenasy, P., and Révai, A., *Z. Elektro. hem.*, **19**, 344 (1913); Thatcher, C. J., *J. Soc. Chem. Ind.*, **40**, 328 R (1921); McKee, R. H., and Leo, S. T., *J. Ind. Eng. Chem.*, **12**, 16 (1920).

[31] Thompson, M. de K., Thompson, N. J., and Sullivan, A. P., *Met. Chem. Eng.*, **15**, 677 (1916); **18**, 178 (1918).

Products Company at East Chicago, Ind., 49 in a single cell room, are shown in Fig. 20. Operating details are given in Table 17. The electrolyte was fed to each cathode compartment by means of a separate tube. Hydrogen was liberated at the cathode and NaOH generated. The solution circulated around the cathode, discharging at the top to be pumped through a carbonating tower where the NaOH was reconverted to carbonate, and the cycle was repeated. The anolyte entered the

Fig. 20.   Electrolytic cells in white-lead plant of the Anaconda Lead Products Company.   (*American Hard Rubber Company.*)

cell through submerged pipes, circulated about the anodes, and flowed out at the bottom of the cell with its quota of precipitated white lead. The discharge of all cells was pumped to thickeners, the clear liquor returning to the cell. The thickened pulp contained about 30 per cent white lead. It was filtered, the solution being removed by a series of countercurrent washes and returned to the anolyte system. The lead compound was washed in hot water to remove any soluble salts, and was then pumped along with the water to a filter where the moisture was decreased to 35 per cent. The solids went to a drier with an aluminum steam-jacketed hearth, after which they were pulverized, packed, and barreled for market. Since the particle size was determined in the original precipitation, the pulverizing operation merely

TABLE 17. ELECTROLYTIC WHITE LEAD[1]

Current:
  Current density, amp/sq ft cathode. .:. 30
  Voltage per tank 3 50
  Current, kw per generator   . 864
  Current efficiency, %. 97
  Kwhr/ton white lead...... 450–500
Anolyte:
  Composition..   .... Sodium acetate with a small amount of Na_2CO_3
  Temperature, °C 40
  Circulation, gal/min.............. 16–18
Anodes:
  Composition .. .. Pb 99.87%, Sb 0.012, As 0.0005, Cu 0.0004, Zn 0.0029, Bi 0.111; Ag 0.29 oz per ton
  Length, width, thickness.......... ... $30\frac{1}{2}'' \times 21'' \times 1''$
  Weight, lb. .   .... :.... .. 250
  Mode of suspension.... .. .. Cast lugs
  Life, hr 85
  Pounds scrap   75
  Percentage scrap....... 30
Catholyte:
  Composition ... . Sodium acetate with large amount of Na_2CO_3
  Circulation, gal/min.............. . 3 5
Cathodes:
  Material......   . . . . Steel plate
  Length, width, thickness.....   .. . $31'' \times 22\frac{3}{8}'' \times 16$ gage
  Mode of suspension.. .   ... Side and bottom supports
Diaphragms......   . ... Heavy linen duck
Deposition tanks:
  Length, width, depth. ...   . $54'' \times 24\frac{1}{2}'' \times 33\frac{5}{8}''$, hopper bottoms
  Material of construction .   .. .. . Reinforced concrete
  Number anodes, cathodes 18, 19
Anodé slime:
  Percentage anode......... .... 0.4
  Composition................... . . Ag 33.3 oz per ton; Pb 66.17%, Sb 1.86, As 0.08, Cu 0.06, Zn 0.40, Bi 10.35
  Removed........................... Every 12 hr
White lead:
  Thickener feed, % solids............... 0.50
  Thickened pulp, % solids...... ... .. 25.0
  Washed filter cake, % solids... .... 55.00
  Dried product, % moisture............. 0 20 (max)
  Drier temperature, max, °C......   .. 120
  Analysis......................... Total Pb 80.14, total CO_2 11.35

[1] BURROWS, D. G., *Trans. Am. Inst. Mining Met. Engrs.*, **73**, 146 (1926).

crushed small lumps that may have been formed in the drying stage.

Lead of practically any composition may be used for anodes in this process without affecting the purity or quality of the white lead produced. Metals other than lead in the anodes were recovered in the form of a slime which adhered to the anode surface, recovery being effected by removing the anodes at regular periods and scouring the surface clean. The frequency of removal was determined by the amount of slime-forming
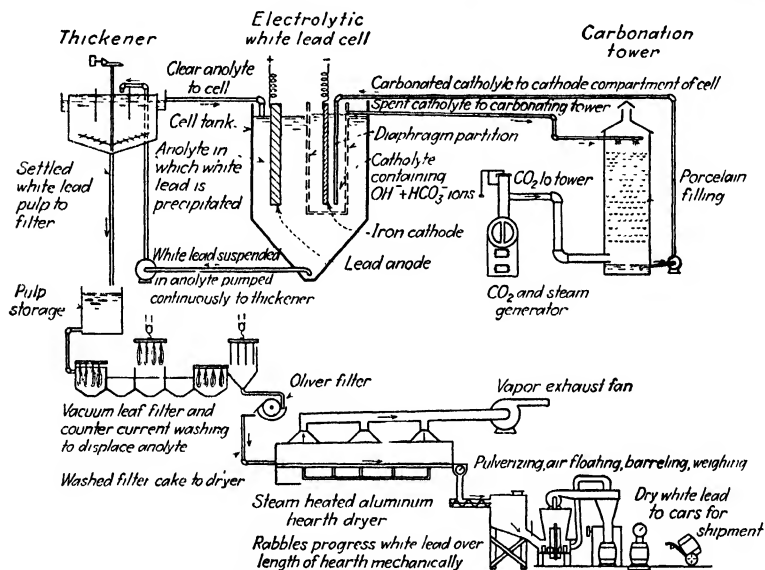

FIG. 21.   Flow sheet of electrolytic white-lead process.   (*Anaconda Lead Products Company.*)

material present and was based on two considerations: the increase of internal resistance of the cell and consequent power loss with accumulation of slime, and the insoluble anode action of an electrode coated with slime, resulting in the decomposition of sodium acetate.

The flow sheet in Fig. 21 gives the operations.

Cadmium Yellow.   Cadmium yellow of a brilliant and permanent color has been experimentally produced electrolytically[32] in a two-compartment cell.   Ferrous sulfide served as the

[32] Fink, C. G., and GROSVENOR, W. M., *Trans. Am. Electrochem. Soc.*, **58**, 475 (1930).

source of sulfur, and the electrolyte was a weakly acid solution of an alkali sulfide. The cell voltage was 0.2 to 0.5. A finely divided iron powder was produced as a by-product. The CdS was precipitated in the anode compartment and the FeS dissolved in the cathode compartment, while the iron and other metallic impurities deposited on the steel cathode as a solid plate or as a fine slime. Sticks of electrolytic cadmium served as anode.

Electrolytic Cuprous Oxide. Copper is converted to stable cuprous oxide by anodic oxidation of copper in a hot aqueous
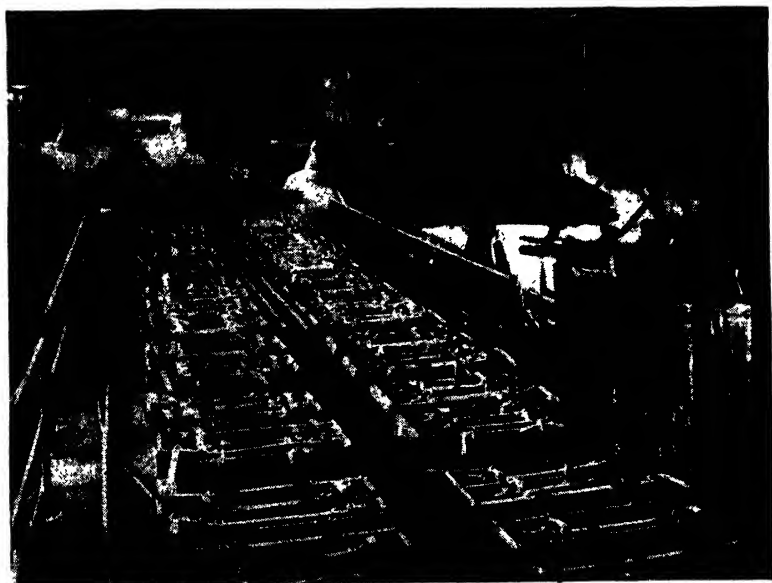
Fig. 22. Plant for electrolytic cuprous oxide. (*Röhm and Haas Company.*)

solution containing at least 4 per cent of an alkali metal halide such as NaCl and a small amount (suitably about 0.1 per cent) of a lyophilic protein colloid such as glue. The precipitated copper compound is washed and is treated with a solution of a lyophilic protein-containing colloid such as glue, and the compound is dried, being then suitable for preparing fungicidal and antifouling compositions.[33] A commercial plant is shown in Fig. 22.

[33] HURD, L. C. (to Röhm & Haas Co.), U.S. Patent 2,273,643 (1942); Röhm & Haas Co., British Patent 533,931 (1941).

Cuprous oxide was deposited cathodically by Stareck.[34]   Fink and Adler[35] found deposits of this type to be photoactive in their studies of semiconductor photocells and to be more reproducible than those made thermally.

Mercuric Oxide.[36]   Mercuric oxide for use in catalysts for acetaldehyde was made by electrolytic oxidation.

Mercury is the anode in an alkaline electrolyte consisting of 80 g per liter Na_2CO_3, 40 g per liter $NaOH$, 5 g per liter $NaCl$, and 1 g per liter goulac.   The cell body consists of a steel tank 100 in. long by 56 in. wide with straight sides 27 in. high.   The bottom slopes from the vertical sides to a 4-in. pipe opening in a vertical distance of 46 in.   A concrete tray 80 in. long by 20 in. wide by 2 in. deep with 2-in. walls is hung horizontally about 16 in. below the top of the cell.   This concrete tray holds the mercury. The perforated cast-iron cathode is suspended over the tray.

An oxide layer forms on the mercury surface.   This is continuously skimmed off along with some occluded mercury which falls to the sloping bottom of the cell.   A concrete scraper is fastened to the middle of the cathode on its underside.   It dips into the tray and runs the full length of it.   The cathode and scraper are supported on a framework that is rolled back and forth across the tray 12 to 15 times per hour.   The scraper pushes accumulated oxide ahead of it and over the edge of the tray.

The accumulated material in the bottom of the cell is drained out along with electrolyte into a tank with a stirrer, where the droplets of mercury can coalesce and run out of a trap in the bottom of the tank.   The suspended mercury oxide is pumped to a filter press to recover the oxide.   The filter cake contains 52 per cent oxidized mercury and 26 per cent free mercury.   The filtrate from the process is diluted with water to make up for that lost by evaporation and electrolysis, and returned to the cells.

Positive current is conducted to the mercury by steel plates dipping into the mercury at each end of the tray.   The anode leads are rubber-covered where they go through the electrolyte.

[34] STARECK, J. E., U.S. Patents 2,081,121 (1937); 2,313,454 (1943).

[35] FINK, C. G., and ADLER, E., *Trans. Electrochem. Soc.*, **79**, 377–412 (1941).

[36] GARDINER, W. C., Technical Industrial Intelligence Branch, U.S. Department of Commerce, *FIAT Final Rept.* **822** (PB 37,781).

The cells operate at 1,600 to 1,800 amp so that the anode current density is 17 to 20 amp per sq ft. The nominal distance between anode and cathode is less than 1 in., but this varies according to the amount of mercury in the tray.

When the voltage goes up to 17, mercury is added until the voltage drops to 12. Cells operate at 50 to 55°C. Power consumption is of the order of 4.2 to 4.4 kwhr per kg or 2 kwhr per lb HgO.

Manganese Dioxide. In the electrolysis of manganous sulfate solution with nonattackable anodes, the latter are coated with deposited MnO_2. First divalent manganese ion is oxidized to tetravalent manganese ion:

$$MnSO_4 + SO_4 + 2\oplus = Mn(SO_4)_2$$
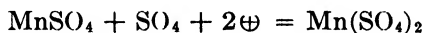
The manganic sulfate then decomposes hydrolytically into manganese dioxide and sulfuric acid:

$$Mn(SO_4)_2 + 2H_2O = MnO_2 + 2H_2SO_4$$
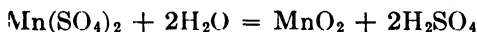
This deposit of MnO_2 has a structure adapted to use as a depolarizer in dry cells. Nichols,[37] carrying out tests for the Burgess Battery Co., made his manganous sulfate by leaching a rhodochrosite ore ($MnCO_3$) with sulfuric acid and then removed iron from the solution.

The electrolyte contained 100 g per liter of $MnSO_4$ plus 33.5 g of H_2SO_4. The current density was 0.6 to 1.0 amp per dm^2 (5.57 to 9.29 amp per sq ft), the temperature about 90°C. With an electrode spacing of 2.5 cm (1 in.), the bath voltage was 2.5 volts. The solution should be exhausted down to only 50 g per liter of $MnSO_4$ plus 67 g of H_2SO_4. The cell solution is then regenerated by leaching more rhodochrosite, so the sulfuric acid is used cyclically.

Nichols used graphite cathodes and hard lead anodes with at least 5 per cent Sb. The MnO_2 formed on the anodes in a coherent layer, which could reach as much as 6 mm (0.24 in.) thick and was stripped. With a current efficiency of 70 per cent, the energy consumption was 2.16 kwhr per kg of MnO_2 (0.982 kwhr per lb).

Marx,[38] who checked Nichols' work but with platinum anodes,

[37] NICHOLS, G. W., *Trans. Electrochem. Soc.*, **62**, 393–403 (1932).

[38] MARX, PETER, *U.S. Bur. Mines Inform. Cir.* 7464, May, 1948.
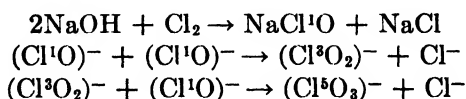
found the best operating conditions to be:

Temperature..................	80°C
Voltage..........................	3
Current density.	0.5–1 amp/dm² (4.65–9.29 amp/sq ft)
Current efficiency........... ..	65–70 %
Energy consumed..........	2.4 kwhr/kg MnO₂ (1.09 kwhr/lb)
MnO₂ in product...	92 %
Total Mn as MnO₂ in product... .	94 %

The product made on platinum anodes is suitable for dry cells. With a graphite anode, current efficiency is 55 per cent, and corrosion of the anode cannot be avoided.   With a hard lead anode, the current efficiency is 55 per cent, and in addition the product is so contaminated with lead that the life of a dry cell is shortened.

Chlorates.   Sodium chlorate finds considerable application as a weed killer.   The electrolysis of halide solutions with the production of chlorates may be considered the result of a series of complex reactions dependent upon temperature, acidity, addition agents, anode and cathode potentials, overvoltages, as well as concentration of electrolyte.   In the production of chlorine and caustic, the anodic and cathodic products of the electrolysis are kept separate.   If, however, they are allowed to mix, hypochlorites result, as

$$Cl_2 + 2NaOH \rightarrow NaClO + NaCl + H_2O$$

The hypochlorite ion, in which the chlorine has a positive valence of 1, may be self-oxidized to a chlorite ion, in which chlorine has a valence of 3, and a chloride ion, and this chlorite ion in turn is further oxidized by hypochlorite to a chlorate ion in which chlorine has a valence of 5.

$$2NaOH + Cl_2 \rightarrow NaCl^1O + NaCl$$
$$(Cl^1O)^- + (Cl^1O)^- \rightarrow (Cl^3O_2)^- + Cl^-$$
$$(Cl^3O_2)^- + (Cl^1O)^- \rightarrow (Cl^5O_3)^- + Cl^-$$

If the electrolysis be considered from the starting point of NaCl in which the chlorine has a valence of -1, the valence changes necessary for the production of chlorate would be from -1 to $+5$, or a total of 6, indicating that 6 F per equivalent of chlorate would be required.

When an alkaline solution of a halide is electrolyzed without

a diaphragm, chlorine at the anode reacts to form hypochlorite ions whose concentrations increase. Inasmuch as the hypochlorous acid decreases, the chlorite ion is more readily discharged. Chlorates may be formed and oxygen evolved more readily than in a neutral solution and at a lower hypochlorite concentration. The effect is increased by the addition of more alkali and finally chlorate production and oxygen evolution consume almost all the current. With the addition of further amounts of alkali, oxygen evolution increases and the chlorate production diminishes as the result of OH^- ion discharge.

When an acid solution of a chloride is electrolyzed, quite a different process occurs. At first the mixing of anolyte and catholyte produces a hypochlorite solution containing a little free $HClO$. If some free mineral acid be added, the $HClO$ concentration is increased as well as the oxidation of the $HClO$ by ClO^- ions to produce chlorates, chlorine, and hydrogen. The H^+ ions liberated give more $HClO$, and the process continues with the formation of chlorate in all parts of the electrolyte. The velocity of the reaction varies with temperature, being slow at 20°C but rapid at 70° or over. Temperature will have a greater effect on the formation of chlorate than does the ClO^- ion discharge. One hundred per cent current efficiency without the evolution of oxygen at any stage of the process should be possible if cathodic reduction be avoided by the addition of a chromate, and ClO^- ion discharge should be entirely prevented. Current efficiencies of 85 to 90 per cent can be obtained with smooth platinum anodes and up to 99 per cent using platinized platinum. Magnetite anodes give lower efficiencies. The current efficiency is materially affected by the current concentration. The chemical formation of chlorate takes place not only in the areas adjacent to the electrodes, but throughout the whole cell. For a given rate of formation of ClO^- ions and a given current passing through the cell, increasing the volume of electrolyte increases the current efficiency.

The first chlorate production in the United States was based on the patents of Gibbs[39] and reported by Richards.[40] Platinum anodes were used. These have been replaced in the present-day larger cells by graphite of the impregnated type. Operating

[39] GIBBS, W. T., U.S. Patents 665,426–7, 665,679 (Jan. 8, 1901).

[40] RICHARDS, J. W., *Electrochem. Ind.*, **1**, 19 (1902).

data[41] for a modern potassium chlorate plant are given in Table 18, column 1.

In general, chlorate cells are iron tanks which are often completely or partially concrete lined. Cell voltages with graphite anodes and iron cathodes are lower than with platinum. The electrolytes usually contain some potassium or sodium dichromate and are acidified and their pH controlled. Saturated solutions of chlorides are the raw materials. Some typical operating data are given in Table 18, column 2, and the work of Groggins
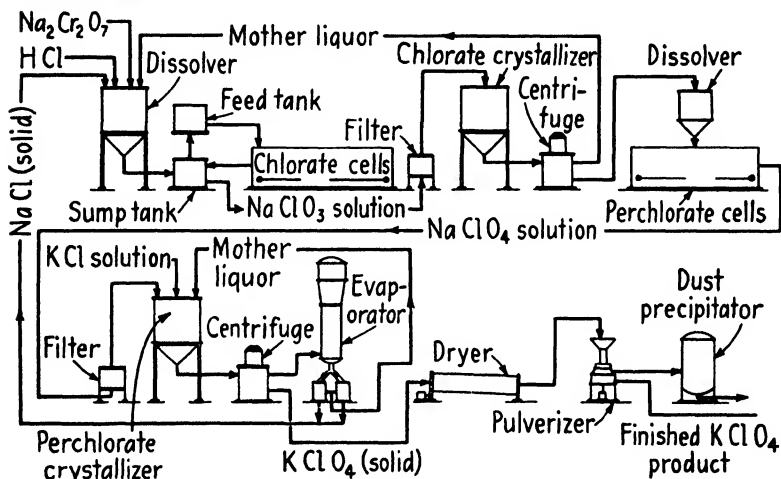
Fig. 23.   Flow sheet for chlorate and perchlorate production.

and his associates in their study of the electrochemical production of sodium chlorate[42] in the Department of Agriculture is given in column 3. The operating data for large cells are given in column 4. A flow sheet for chlorates and for perchlorates made from chlorates is given in Fig. 23. Figure 24 illustrates an American chlorate cell room.

The raw material, salt (NaCl), is usually purified to free it of heavy metals and magnesium and calcium compounds. These may form thick oxide layers on the cathode and increase the cell resistance. The electrolyte is always yellow as the result of the presence of chromate which aids in regulating the H^+ ion

[41] WHITE, N. C., *Trans. Electrochem. Soc.*, **92**, 15–21 (1947).

[42] GROGGINS, P. H., PITMAN, A. L., McLAREN, J., and DAVIS, F. H., *Chem. & Met. Eng.*, **44**, 302 (1937); **45**, 692 (1938).

TABLE 18. CHLORATES

	(1)	(2)	(3)	(4)	(5)	(6)
Product	KClO₃	NaClO₃	NaClO₃	NaClO₃	NaClO₃	NaClO₃
Cell:						
Material of construction	Steel				Steel	
Length × width × depth	20″ × 30″ × 48″ high (50.8 × 76.2 × 122 cm)				43″ × 30″ × 42″ high (109.2 × 76.2 × 106.7 cm)	
Capacity					200 gal (757 l)	
Electrolyte g/l:	250 KCl, 50 KClO₃,	Saturated NaCl	300 NaCl	Saturated NaCl	250 NaCl	Saturated NaCl
Na₂Cr₂O₇, g/l	2 K₂Cr₂O₇		2 4		2	
pH	6 9	2-3	6 6		6 8	
HCl	2(K₂Cr₂O₇)	1 2-1 4				
Temperature, °C	25-70 (usually 35-45)	Below 40			35 average	75
Current per cell, amp	3,000	10,000-15,000	650-1,300	2,000-10,000	1,600	5,000
Current density anode, amp/sq ft	10-150 (1-16.2 amp/dm²)	18-45	17 6-22	9 2-23 0	50 (5.4 amp/dm²)	
Current density cathode, amp/sq ft	10-50 (1-5.4 amp/dm²)	9-12	9 2-11 2	9 2-23 0		
Current efficiency, %		80	82	82-84	85-90	
Voltage per cell	3	3 6	2 8-3 6	2 8-3 3	3 1-3 5	2 8-3 5
Energy efficiency, %		30	30+	6c 64		
Energy, kwhr/lb		2 4-3	2 6	2 4-2 6		
Lb/kwhr		0 33-0 41	0 38	0 38-0 41		
Anode:						
Material	Treated graphite	Graphite	Graphite	Graphite	Graphite	Graphite
Size	2″ × 8′ × 48″ (5 × 20 × 76 2 cm)				10 anodes, 1″ × 7″ × 40″ (2 54 × 17.8 × 101.7 cm)	
Consumption, lb/ton product		20-30	26-37	2-3	20 (10g/kg)	
Life, years					1	
Cathode:						
Material	Steel	Iron	Iron	Iron	Steel	Iron
Average operating period of cell, days			20-30			
Raw materials	KCl	NaCl	NaCl	NaCl	NaCl	NaCl
Concentration of chlorate, final, g/l		500-750	505		450-550	
Concentration of chloride, initial, g/l	250	300	300		250	
Concentration of chloride, final, g/l		120	85-100		85	
Material yield, %		90-95	95+			

concentration of the cell so that rapid chemical formation of chlorate occurs. Chromates also passivate the iron portions of the cell.

In commercial operation the chlorate may be formed by the batch method, or else the electrolyte is circulated continuously. In the preparation of potassium chlorate, saturation is reached, the solutions are allowed to crystallize, and the mother liquor,
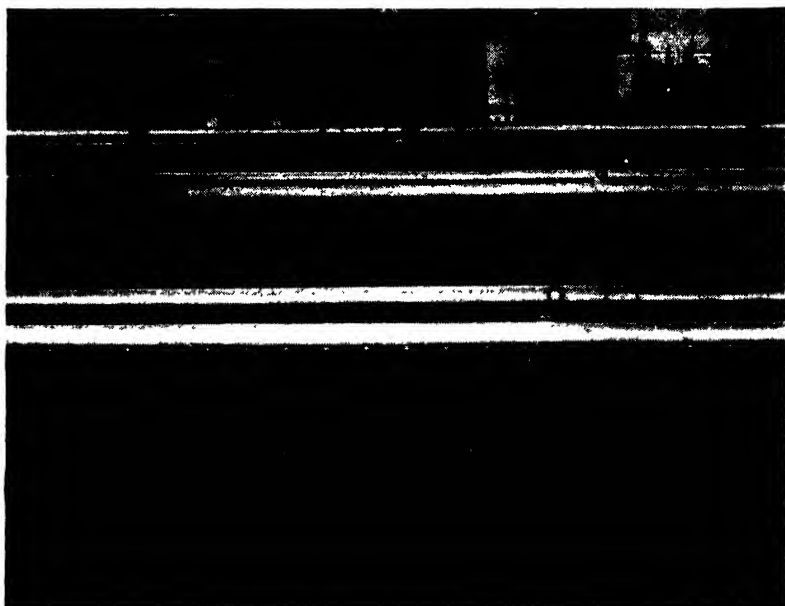

Fig. 24. Chlorate cells. (*Western Electrochemical Company.*)

after resaturation with KCl, is returned to the cells. Sodium chlorate has greater solubility, so that solid salt or saturated solutions are continuously added until the chlorate concentration has reached about 750 g per liter, after which it is allowed to cool and this product is crystallized out. In some plants, however, the liquors containing appreciable amounts of chlorate are evaporated, the NaCl precipitated out and returned to the cells, and the chlorate allowed to crystallize out on cooling.

In some designs the cell body is large, and the volume of the anodes and cathodes is a small fraction of the volume of the electrolyte. In these designs the body is usually steel or iron, lined with brick to prevent corrosion. In other designs prac-

tically the entire cell body is taken up by anode and cathode and, except for a small space at the bottom usually provided for settling out of eroded graphite particles, the electrolyte volume is restricted to the spaces providing clearance between the elec-
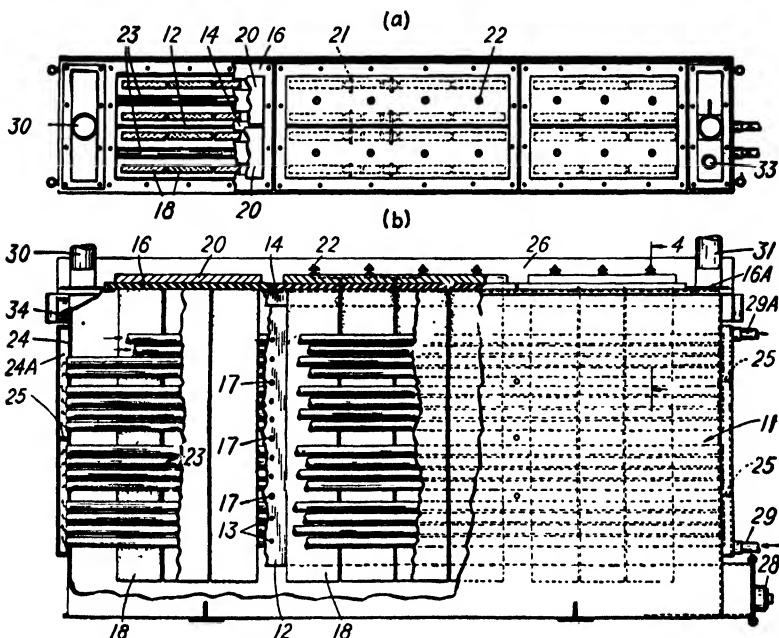
FIG. 25. Chlorate cell (5,000 amp). Cells connected in series to make 360-volt circuits. (*Western Electrochemical Company*)

11. Steel tank cathode
12. Steel cathode partition
16. Artificial stone cover plate
18. Graphite anodes
20. Lead block
22. Stud bolts (electrical terminals)
23. Cooling-liquid tubes (steel)

24a. Cooling-liquid manifold
25. Cooling-liquid baffles
26. Cathode connecting bar
28. Drain
29. Cooling-liquid inlet
29a. Cooling-liquid outlet
30. Gas outlet

trodes. These spaces are usually from 0.25 to 0.5 in. (0.6 to 1.2 cm) when new anodes are first installed. Current concentrations therefore vary from 50 to 400 amp per cu ft (1.7 to 14 amp per dm³).

American electrolytic sodium chlorate manufacture is described.[43] Cell construction is shown in Fig. 25.

Solar salt is unloaded into large tanks and converted into a saturated water solution. Purification follows by precipitation and settling of

[43] *Chem. & Met. Eng.*, **51**, 130 (November, 1944).

calcium , and magnesium impurities. The solution is clarified by filtration and fed to banks of electrolytic cells operating at 500 to 600 volts per series with current ranging from 2,000 to 3,500 amp. Power entering at 11,000 volts is stepped down by means of transformers and then converted to direct current by mercury arc rectifiers.

The formation of sodium chlorate by electrolysis of a brine solution is complex and is the culmination of a series of electrochemical and chemical reactions. Maintenance of high operating efficiencies depends on a number of factors such as temperature, hydrogen ion concentration, addition agents, etc. Usual current densities for producing sodium chlorate range from 74 to 185 amp per sq ft giving an operating temperature of 85 to 90°C. During this phase it is necessary to add sodium chloride continuously as sodium chlorate is quite soluble.

Cell liquors after electrolysis are clarified by filtration and fed to a two-stage evaporator for concentration, after which separation occurs in crystallizers with the sodium chlorate crystals passing to refining tanks for treatment. Final separation is obtained by use of batch centrifuges. The mother liquor is returned to the cell feed tanks for adjustment to final strength and volume. Drying of the crystals takes place in heated air rotary driers from which the material passes to grinding, screening, and packing operations all of which are protected by dust control equipment.

Cathode current densities vary from 10 to 50 amp per sq ft (1 to 5.4 amp per dm^2). Anode current densities vary more widely from 10 to 150 amp per sq ft (1 to 16.2 amp per dm^2). Increasing the current densities tends to increase the voltage drop across the cell and reduce power efficiency. It also increases the rate of attack on graphite anodes per unit of time, but within limits decreases the graphite consumption per pound of chlorate produced.

Current efficiency improves as the temperature is lowered in the range of from 70 to 30°C, but the voltage increases. The chemical production of chlorate by conversion of the hypochlorite produced in the cells is slowed by the reduction in temperature. Graphite consumption decreases quite rapidly at first with a decrease in temperature, and a balance between these factors has to be established. Individual operators pick their own optimum point for this balance at some spot from 25 to 70°C. The majority in the United States probably operate within the range of 35 to 45°C, since graphite losses at 60 to 70°C are more than sufficient to offset any advantages. Some European production is

carried on at this figure (70°C) using magnetite anodes which have not yet been produced in quantity in the United States.

The current efficiency for $KClO_3$ formation is 90 per cent or greater, and for $NaClO_3$ 80 per cent. On the basis of a cell voltage of 3.6, the energy expenditure is 2.4 to 3 kwhr per lb, the lower figure representing more average practice. If the theoretical voltage be taken as 1.43,[44] the theoretical energy per pound of $KClO_3$ is about 0.85 kwhr per lb. The energy efficiency then becomes 35 per cent on the basis of an expenditure of 2.4 kwhr per lb $KClO_3$ and less than 30 per cent when a figure of 3 kwhr per lb is taken.

Bromates. Bromates are made by electrolysis of bromides in cells of related design to those employed for chlorates. Corrosion of cell structure may be more severe than in the case of chlorates.

Perchlorates. Perchlorates are used in the form of potassium and ammonium salts for pyrotechnics and explosives. Since sodium chlorate is so readily soluble, it is the one usually prepared by electrolysis, but, inasmuch as it is deliquescent, it is converted into potassium and ammonium salts by reaction with the corresponding chlorides.

If the anode potential be high enough, the chlorate ion may be oxidized to the perchlorate with good current efficiencies. The valence change of chlorine is from 5 to 7, and therefore 2 F per equivalent of perchlorate are required. Neutral or faintly acid solutions of 60 to 70 per cent sodium chlorate are preferred in practice. The production of alkalinity during electrolysis causes a decrease in the current efficiency. Electrolyte circulation must be effective to maintain good current efficiencies. Operating data are given in Table 19. Cooling systems are employed for control of temperature either in the cell or in the electrolyte circulating system, as is the case with chlorates. French plants employ a concentrated solution of sodium chromate and a saturated solution of sodium chlorate for the successful production of perchlorates. The action is similar to that produced by a little chromate in the electrolyte during the production of chlorates. Figure 26 shows an American perchlorate cell room, while Fig. 27 shows the cell construction in a diagrammatic fashion.

[44] LUTHER, R., *Z. Elektrochem.*, **8**, 601 (1902).

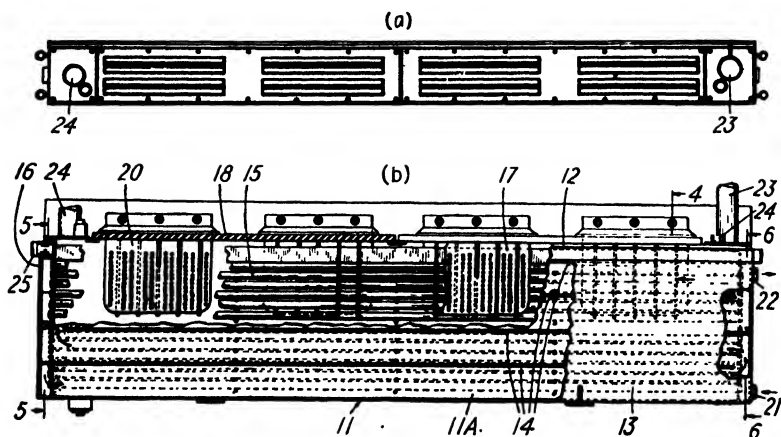Fig. 26.　Perchlorate cells and driers.　(*Western Electrochemical Company.*)

(a)

24　　　　　　　　　　　　　　　　　　　　　23

16 24　　20　　　18 15　　(b)　　　17　　12　　4　　23
5　　　　　　　　　　　　　　　　　　　　　　　24
　　　　　　　　　　　　　　　　　　　　　　　6
25　　　　　　　　　　　　　　　　　　　　　22
5　　　　　　　11　　11A　14　　13　　21　6

Fig. 27.　Perchlorate cell (5,000 amp).　Cells connected in series to make 360-volt circuits.　(*Western Electrochemical Company.*)

11. Steel tank cathode	18. Cover plates (artificial stone)
12. Cover flange	21. Cooling-liquid inlet
13. Cooling-liquid jacket	22. Cooling-liquid outlet
14. Cooling-liquid jacket partitions	23. Gas outlet
15. Cooling-liquid tubes	24. Electrolyte inlet (tube leading to 2 in.
16. Cooling-liquid manifold	from bottom not shown)
17 and 20. Platinum anodes	25. Electrolyte outlet

TABLE 19. PERCHLORATES AND PERCHLORIC ACID

	(1)	(2)	(3)	(4)	(5)
Product	$NaClO_4$	$NaClO_4$	$NaClO_3$	$NaClO_4$	$HClO_4$
Cell:					
Material of construction		Sheet steel	Steel	Steel	
Length × width × height		30″ × 16″ × 33″ (76.2 × 40.6 × 83.8 cm)	8'6″ × 5″ × 2'0″	8'6″ × 5″ × 2'0″	
Capacity			5.9 cu ft	5.9 cu ft	
Electrolyte g/l.:	60–70 $NaClO_3$	650–700 $NaClO_3$	600 $NaClO_3$	90–110 $NaClO_3$	0.5N HCl
$Na_2Cr_2O_7$, g/l.			5	5	
Temperature, °C	30–60	45–55 (av.)	40–45	40–45	18
Circulation, gal/min		1–2	2	2	
Current per cell, amp	270–480	500	5,000	5,000	150
Current density anode, amp/sq ft		480 (52 amp/dm²)	288 (31.1 amp/dm²)	288 (31.1 amp/dm²)	15
Current density cathode, amp/ sq ft.			72 (7.7 amp/dm²)	72 (7.7 amp/dm²)	
Current efficiency, %	80–85	93–97	90	70	
Voltage per cell, v.	5–6.5	6.2–6.8	6.8	6.8	8
Energy efficiency, %	1.6		14.4	11.4	11.8 (60% acid)
Energy, kwhr/lb	0.62		1.5	1.9	0.085
Lb/kwhr.			0.66	0.52	
Anode:					
Material	Platinum	4 Pt-clad Cu rods	Perforated Pt sheet	Perforated Pt sheet	Platinum
Size		0.5″ diam × 30″ long (1.27 × 76.2 cm)			
Consumption,			0.2 troy oz/ton	0.2 troy oz/ton	
Cathode:					
Material	Iron	4 steel tubes	Steel	Steel	Copper or silver
Size		3″ diam × 33″ long (7.6 × 83.8 cm)			
Average operating period of cells, days			Indefinite	Indefinite	
Raw materials	$NaClO_3$	$NaClO_3$ solution	$NaClO_3$	$NaClO_3$	HCl
Concentration of perchlorate, final, g/l.		800	500	580–600	20 $HClO_4$
Concentration of chlorate, initial, g/l.	650		600		
Concentration of chlorate, final, g/l.		650–700	90–110	90–110	
Material yield, %	5	20		5	30–40

Perchloric Acid. Chlorides such as HCl may be electrolytically converted to perchloric acid on a commercial scale.[45] The operating data are given in Table 19, column 5. The product of the cells containing small amounts of HCl and chloric acid and between 25 and 30 g of perchloric acid per liter was evaporated in fused silica to produce the 60 per cent perchloric acid of commerce.

[45] Goodwin, H. N., and Walker, W. H., *Chem. & Met. Eng.*, **25**, 1093 (1921); U.S. Patents 931,944, and 1,271,633.

CHAPTER 8

CORROSION

The majority of investigators would probably agree that the most destructive types of corrosion are those of an indirect electrochemical character. Except in a few instances direct chemical attack on metals forms reaction products on the surface of the metal which retard the attack more and more as the reaction product accumulates. Thus, when a metal is heated in air, it becomes covered with an oxide scale which in most cases tends to protect the metal from further attack, save where the oxide layer is porous, flakes off, or shows cracks. When the reaction product is either volatile or liquid, direct chemical action may cause marked corrosion.

When two dissimilar metals are in contact with an electrolyte, a galvanic couple is formed and a potential set up. The metal at the higher potential will become the anode and tend to go into solution and will therefore corrode. The magnitude of the potential will affect the rate of corrosion. Galvanic couples may be formed in an alloy containing dispersed compounds or alloy constituents, or metals containing inclusions, or in two pieces of the same metal in contact when these have had different thermal histories such as heat treatment or have been subject to different mechanical stresses due to working or fabrication.

The simplest known form of an electric cell consists of two metals connected with each other and immersed in a conductive solution. The results of such a couple are well known: one metal is shielded while the other is attacked rapidly. Whenever two metals are in contact with each other in the presence of moisture, a similar situation is created.

The rate of corrosion varies with different combinations of metals, and experimentation has made it possible to list the various metals in order of their susceptibility to this type of corrosion. The metal which sacrifices itself is the anode, while the protected metal is the cathode. By choosing metals which

137

fall in the same group, the tendency toward this two-metal galvanic action is greatly reduced. Table 20 should make it evident why cadmium and zinc, which are so close to aluminum in potential, are so widely used in aircraft, where steel members almost invariably contact aluminum alloys.

TABLE 20. GALVANIC SERIES

Corroded end (anodic)
  (*Least noble*)
    Magnesium and magnesium alloys
    Zinc
    Aluminum and noncopper-bearing alloys
    Cadmium
    Aluminum alloys (copper bearing)
    Mild steel
    Wrought iron
    Cast iron
    Ni-Resist
    13% chromium stainless steel, type 410 (active)
    50–50 lead-tin solder
    18:8 stainless steel, type 304 (active)
    18:8:3 stainless steel, type 316 (active)
    Lead
    Tin
    Muntz metal
    Manganese bronze
    Naval brass
    Nickel (active)
    Inconel (active)
    Yellow brass
    Admiralty brass
    Aluminum bronze
    Red brass
    Copper
    Silicon bronze
    Ambrac
    70–30 copper nickel
    Comp. G-bronze
    Comp. M-bronze
    Nickel (passive)   .
    Inconel (passive)
    Monel
    18:8 stainless steel (passive)
    18:8:3 stainless steel (passive)
Protected end (cathodic)
  (*Most noble*)

The rate of corrosion is accelerated as the distance apart in the table is increased. Any metal in the series will protect any metal beneath it and will tend to accelerate the corrosion of any metal above it. Relative position within each group may vary with the corrosive condition, but it is fairly certain that the sacrificial-protection effect between groups can be relied upon to act as indicated.

An electrochemical theory of corrosion was first suggested by Whitney[1] and Cushman,[2] based on the Nernst theory of electrolytic solution pressure. If iron, for example, were in contact with a metal having a lower electrolytic solution pressure, the iron would dissolve and hydrogen would be deposited on the material of lower electrolytic solution pressure which would function as cathode. Walker[3] suggested that the quantity of iron which could dissolve in water in the absence of oxygen was probably limited to the amount necessary to polarize the cathodic portions of the metal. If the water contained an oxidizing depolarizer or oxygen, the hydrogen could be removed from the cathodic portions and corrosion continue indefinitely.

The early electrochemical theories did not explain the local and apparently capricious nature of corrosion. They failed to explain why sometimes corrosion produces in its early stages a compact and continuous layer which stops the attack, while at other times the product is of a porous or flocculent nature which seems to stimulate the attack. The earlier theories failed to account for the phenomenon of pitting. They did not show why corrosion should proceed more quickly at the bottom of a deep pit than elsewhere, for such a place would be expected to be inaccessible to oxygen and corrosive agents. Aston[4] showed that wet rust promoted further rusting because it acted as a diaphragm, screening the underlying metal from the direct access of oxygen. When two pieces of iron are immersed in the same liquid and one is exposed to the action of dissolved oxygen and the other shielded from it by wet rust, the shielded electrode becomes the anode.

[1] WHITNEY, W. R., *J. Am. Chem. Soc.*, **25**, 394 (1903).

[2] CUSHMAN, A. S., *U.S. Dept. Agr. Bull.* 30, Office of Public Roads (1907); *Proc. Am. Soc. Testing Materials*, **7**, 211 (1907).

[3] WALKER, W. H., CEDERHOLM, A. M., and BENT, L. N., *J. Am. Chem. Soc.*, **29**, 1251 (1907).

[4] ASTON, J., *Trans. Am. Electrochem. Soc.*, **29**, 449 (1916).

Evans[5] has shown that galvanic couples may be set up by differential aeration of many metals.   The explanation is thus found in the fact that corrosion takes place to a greater degree at those places to which oxygen has least direct access.   When a metal is immersed in water and some parts exposed to the action of dissolved oxygen while others are protected, thin films of oxide or hydroxide are produced on the part to which oxygen has access. These protect or ennoble that part of the surface.   Currents are then set up between other portions of the metal to which the oxygen has no access and the ennobled aerated portions.   The former constitute the anode and are corroded, while the latter are cathodic and thus comparatively immune from attack.

An essential condition for electrochemical corrosion is some departure from uniformity, such as in a metallic article of heterogeneous character, on a coarse scale through contact of dissimilar metals, and on a fine scale through contact of alloy constituents, or by the unequal access of oxygen to different parts of the metallic article.   Evans[6] explains the rusting of steel as follows:

Experiments have shown that the places where oxygen concentration is least are anodic and suffer corrosion; thus, although oxygen is needed for the action, the attack occurs at places to which oxygen has no direct access.   For instance, a drop of brine placed on a steel plate causes corrosion below its center; but near the edge of the drop, where oxygen has best access to the metal, there is no attack at all.   Similarly a vertical steel sheet, partly immersed in brine, suffers corrosion in the lower part; the aerated (cathodic) zone immediately below the water level remains quite uncorroded for a considerable time.   Here the direct action of oxygen will be to produce a thin oxide film over the upper part of the metal, and although this film would be probably incapable of protecting the metal if it existed over the whole surface, it will be sufficient to divert the corrosion on to the lower part where oxygen is deficient.   This "diversion" of the attack occurs in the following way: the potential at the oxidized part near the water level is different from that at the relatively oxide free part below, and the "differential aeration currents" set up will cause corrosion at the lower portions, yielding ferrous chloride.   That salt, where it meets the $NaOH$ from the cathodic

[5] EVANS, U. R., *Trans. Faraday Soc.*, **18**, 1 (1922); **19**, 201 (1923); **19**, 789 (1924); *J. Inst. Metals*, **30**, 239 (1923).

[6] EVANS, U. R., *Chemistry & Industry*, **45**, 504–508 (1926).

area above, will interact to give $Fe(OH)_2$, rapidly oxidizing to brown $Fe(OH)_3$, and a sinuous membrane of rust will appear between the corroded and uncorroded regions.

A number of metals can protect themselves against corrosion either because the insoluble body which forms the primary corrosion product is continuous and nonporous or because protective films are formed in the presence of oxygen.   Most of

TABLE 21. SOLUTION POTENTIALS MEASURED IN SODIUM CHLORIDE SOLUTION

Metal or Alloy	Potential in Volts[1] Measured in a 1 N (5.85%) Sodium Chloride Solution Containing 0.3% Hydrogen Peroxide ($N/10$ Calomel Scale)
Magnesium	−1 73
Zinc..	−1 00
Pure aluminum (99.95+)	−0 85
2S-O aluminum alloy.	−0 83
Cadmium	−0 82
17S-T aluminum alloy..	−0 68
M.ld steel	−0 67
Lead	−0 55
Tin	−0 49
Brass (60–40)	−0 28
Copper	−0 20
Stainless steel (18–8).	−0 15
Monel metal.	−0 10
Silver	−0 08
Nickel	−0 07
Inconel.	−0 04

[1] These values vary somewhat depending on the particular lot of material investigated and on the surface preparation employed.

the corrosion-resistant materials of the self-protecting class are alloys containing Cr, Ni, Co, Al, or Si.   Films containing these elements appear to afford efficient protection although there is a tendency for them to fail in the presence of chlorides.   Solution potentials, which in a measure are the relative tendency to corrode, are given in Table 21 for a number of commercial materials in sodium chloride solutions.   A large literature has been built up on the subject.[7]

[7] CALCOTT, W. C., WHETZEL, J. C., and WHITTAKER, H. F., Corrosion Tests and Materials of Construction, *Trans. Am. Inst. Chem. Engrs.*, Part 1, **15**, (1923); HAMLIN, M. L., and TURNER, F. L., "Chemical Resistance of

Passivity and Inhibition. A metal or alloy is passive if it substantially resists corrosion in an environment where thermodynamically there is a large, free-energy decrease associated with its passage from the metallic state to appropriate corrosion product.[8] Passivity might be considered a resistance to corrosion, and theories have attributed the phenomenon to solid films, especially of oxides, or gas films, especially H_2 or O_2. Mears[9] proposed a theory that passivity may be achieved either by (1) reduction of the open circuit differences between the local anodes and cathodes, (2) increased anodic polarization, (3) increased cathodic polarization, or (4) a combination of these factors.

If corrosion proceeds by an electrochemical mechanism, the steady-state corrosion rate will be the rate at which the sum of all the dissipative effects is equal to the driving force.[10] At equilibrium,

$$E_o = E_a + E_c + E_R + E_R'$$

where E_o = open-circuit potential difference between the local anodes and the local cathodes

E_a = total polarization of the anode areas

E_c = total polarization of the cathode areas

$E_R = IR$, current flowing multiplied by the resistance of the electrolyte between the anode and cathode areas

$E_R' = IR'$ = current flowing multiplied by the resistance of the metal between the anode and the cathode areas

Engineering Materials," Chemical Catalog Company, Inc., New York, 1923; SPELLER, F. N., "Corrosion: Causes and Prevention," 2d ed., McGraw-Hill Book Company, Inc., New York, 1935; EVANS, U. R., "The Corrosion of Metals," Edward Arnold & Company, London, 1924, 1944; *Chem. & Met. Eng.*, **36**, 521–584 (1929); *Trans. Am. Inst. Mining Met. Engrs.*, Inst. Metals Division, 1929; RAWDON, H. S., "Protective Metallic Coatings," Chemical Catalog Company, Inc., New York, 1928; McKAY, R. J., and WORTHINGTON, R., "Corrosion Resistance of Metals and Alloys," Reinhold Publishing Corporation, New York, 1936; BURNS, R. M., and SCHUH, A. E., "Protective Coatings for Metals," Reinhold Publishing Corporation, New York, 1939.

[8] "Corrosion Handbook," H. H. Uhlig, Editor-in-Chief, John Wiley & Sons, Inc., New York, 1948.

[9] MEARS, R. B., *J. Electrochem. Soc.*, **95**, 1–10 (1949).

[10] Compare with chapter by J. C. Warner in R. B. Leighou's "Chemistry of Engineering Materials," p. 424, McGraw-Hill Book Company, Inc., New York, 1942.

E'_R is generally very small and hence may be neglected in most cases. The equation then becomes

$$IR = E_o - (E_a + E_c)$$

and

$$I = \frac{E_o - (E_a + E_c)}{R}$$

Since I is the corrosion current, its magnitude is a measure of the corrosion rate. The variables which can reduce I to a low value will favor low corrosion rates or, in other words, will induce passivity. Reducing E_o, or increasing E_a, E_c, or R are factors which will reduce I and thus cause passivity.

If E_o be reduced, as in more homogeneous pure metals, low corrosion rates may occur as very pure zinc or aluminum in HCl, or passivation of stainless steel by nitric acid through greater homogeneity.

The anodic polarization is made up of a back emf, such as can result from concentration polarization and also of the IR drop through any film barrier on the anodic surface. E_a is therefore equal to $E'_a + IR_a$ where E'_a is a back emf and IR_a is the voltage drop in the anode film. A thin liquid film containing a higher concentration of ions of the corroding metal than the bulk of the electrolyte will give an E'_a of substantial magnitude. If E'_a approaches E_o in magnitude, corrosion will fall practically to zero.

Reduction of corrosion of lead in H_2SO_4 or an aluminum anode in boric acid or gold in various acids, bases, and salts[11] are examples.

The two components of anodic polarization can work together. If a discontinuous film is formed, the anode area will be restricted, causing an increase in E'_a.

The term E_c can be broken up into IR_c and E'_c components. An increase in the value of E'_c can reduce corrosion rates. The resistance of amalgamated zinc to attack by acid may be caused by the high overvoltage of hydrogen on the amalgam surface which increases E_c. Films of gases or liquids on the cathode surface can similarly bring the corrosion reaction almost to a halt; *i.e.*, they can cause passivity. In like manner, solid films will increase R_c and also cut down corrosion. Here again E'_c and IR_c can work together to reduce corrosion.

Mears holds that the generalized mechanism can be applied

[11] HICKLING, A., *Trans. Faraday Soc.*, **41**, 333 (1945); **42**, 518 (1946).

to all cases of passivity which have been studied thus far. Schoenbein[12] and Faraday[13] considered the passivation of iron in nitric acid. In this case the passivation is caused by anodic polarization (E_a). Contact with platinum, which would increase E_a, does not destroy the passivity while contact with zinc, which would reduce E_a by supplying cathodic current, does not destroy passivity. Contact between unpassivated iron and passivated iron results in passivation of both pieces, since increased anodic polarization of the unpassivated iron results. Iron oxidized by heating in air is passive when introduced into nitric acid of a concentration which would cause rapid attack of unheated iron, because the oxide film limits the exposed anodic area of the iron and thus results in an increased E_a, since the anodic current density is higher at any small gaps in the film.

In a sodium chloride solution, austenitic stainless steels are almost completely passive. If any corrosion does occur, it is extremely localized. It has been established[14] that in sodium chloride solution both the local anodes and the local cathodes on the stainless-steel surface polarize appreciably. If either the polarization of the local anodes or that of the local cathodes can be increased, the corrosion rate will be reduced. If the amount of polarization of either the local anodes or that of the local cathodes can be decreased, the breakdown in passivity will become more complete. Additions of ferric chloride to the solution greatly decrease cathodic polarization and also stimulate corrosion (by a factor of 30). This increase in corrosion rate is accompanied by a shift in the potential of the specimen in a cathodic or noble direction.

Cathodic Protection. Any metal, such as a steel pipe or a lead cable sheath or a storage tank, when placed in contact with an electrolytic substance like soil or water, sets up a flow of current similar to that which occurs inside a dry battery. A number of electric circuits are thus created which may follow varied and unpredictable courses through the electrolyte: from the wall of a buried oil or gas pipe line to a fitting of dissimilar metal; from a power or telephone cable to an adjacent conducting structure; between points in contact with different kinds of soil, etc.

[12] SCHOENBEIN, C. T., *Phil. Mag.*, **9**, 53 (1836).

[13] FARADAY, M., *Phil. Mag.*, **9**, 56 (1836).

[14] BROWN, R. H., and MEARS, R. B., *Trans. Faraday Soc.*, **35**, 467 (1939).

A few examples are shown in Fig. 28. There are also situations in which currents are caused to flow from an underground structure as the result of stray currents from nearby electric railway systems. In either case, minute quantities of the metal continuously leave the pipe or sheath at points where the current emerges from the metal (the anodes). This causes pitting and wearing away of the metal at these areas with subsequent failure of pipe or cable.

A way to combat corrosion of the metal at anodic points is to cause a reversal of the current, making the area which is to be protected cathodic instead of anodic. Contact may be made with the metal to be protected by a galvanic anode of a metal which is higher in the electromotive series. Zinc, magnesium, or aluminum being higher on the galvanic scale than iron makes the iron cathodic and has been utilized. An efficient and economic method of countering the corroding current is to cause a direct current to flow from an outside source, through the metal and the electrolyte, in the opposite direction so that the net effect is to make the contacting soil or water anodic and the structure to be protected cathodic, thus entirely eliminating the loss of metal in the area.

This practice is known as "cathodic" or "counterelectrolysis" protection and has been in common usage on petroleum pipe lines since 1910. It has also been applied to a considerable variety of other structures. A continuous and permanent source of low-voltage direct current is needed for operation. Various types of current sources have been utilized: motor-generator sets or copper-oxide rectifiers associated with available alternating current; d.c. generators operated by internal-combustion engines, sometimes in conjunction with storage batteries, and similar expedients. In remote locations, in the absence of a power line, windmills have been used to operate small d.c. generators.

Reversed Corrosion. Fink and Eldridge,[15] in connection with the restoration of antique bronzes, have shown that corrosion can be reversed. The red, green, or brown layers on ancient bronzes are composed chiefly of copper, lead, and tin minerals in the articles which have been attacked by the nitrates and nitrides

[15] FINK, C. G., and ELDRIDGE, C. H., "First Report on the Restoration of Ancient Bronzes and Other Alloys," Metropolitan Museum of Art, New York, 1925.

CORROSION CAUSED BY MIXTURE OF DIFFERENT SOILS
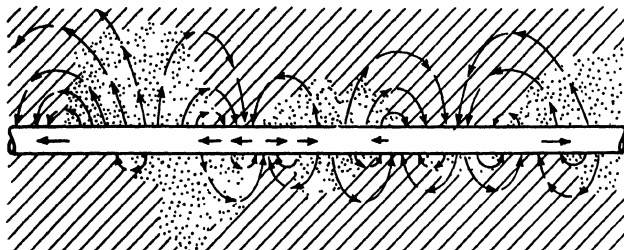
CORROSION DUE TO DIFFERENT TYPES OF SOIL THAT HAVE BEEN MIXED
AS A RESULT OF EXCAVATING AND BACKFILLING, GRADING, RECLAIMING
WASTE LAND

CORROSION DUE TO GALVANIC ACTION OF CINDERS AND ACID FROM CINDERS
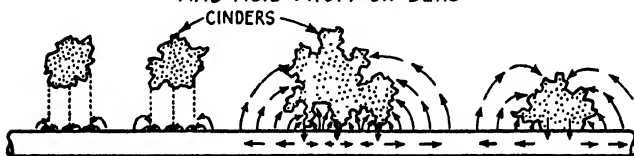
CINDERS

CINDERS IN THE SOIL MAY CAUSE SEVERE CORROSION IN TWO WAYS:
(1) DIRECT CONTACT SETTING UP ACTIVE GALVANIC CELLS
(2) SULFURIC ACID FROM CINDER ABOVE PIPE CARRIED DOWN
THROUGH THE SOIL TO PIPE SURFACE BY SOIL WATERS

CORROSION CAUSED BY SCARRING AND THREADING OF IRON PIPE

SCARS CAUSED BY SHIPPING AND
HANDLING EXPOSE BRIGHT METAL

THREADS EXPOSE BRIGHT METAL

SCARS CAUSED BY STILLSON
WRENCH EXPOSE BRIGHT METAL
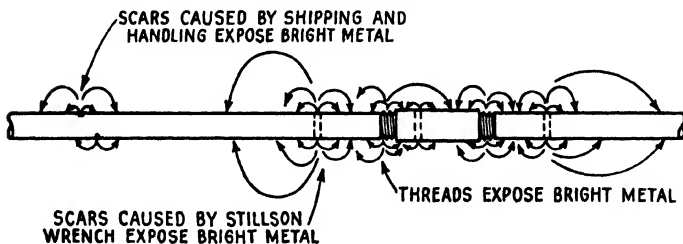
EXPOSED BRIGHT SURFACE IS USUALLY ANODIC TO BALANCE OF
SURFACE - RAPID CORROSION MAY RESULT IN CORROSIVE SOILS

NOTE - A GALVANIZED PIPE WHICH HAS BECOME SCARRED MAY NOT CORRODE
AT SCARS BECAUSE THE ZINC GALVANIZING MAY PROTECT THE METAL
AT THE SCARS.

FIG. 28.   Electrolytic corrosion.   (*The Petroleum Engineer.*)

CORROSION CAUSED BY DIFFERENTIAL AERATION OF SOIL

AIR

AIR

WELL AERATED SOIL

PIPE

— MOIST OR SATURATED SOIL — POOR OR NO AERATION
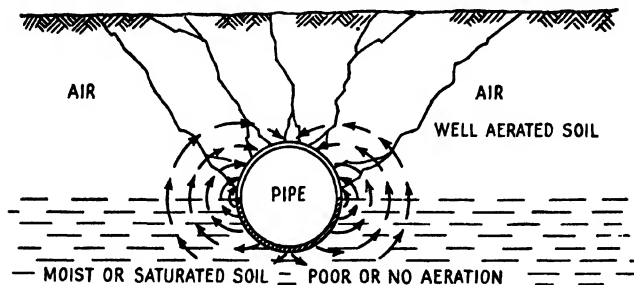
IF AIR DRIES SOIL AT TOP OF PIPE BUT NOT AT BOTTOM, DIFFERENCE IN MOISTURE IN SOIL RESULTS IN CORROSION AS INDICATED ABOVE. DRY SOIL CHANGES METAL-TO-SOIL POTENTIAL MAKING IT LESS NEGATIVE – THIS RESULTS IN GREATER DIFFERENCE IN POTENTIAL BETWEEN BOTTOM AND TOP OF PIPE WHICH TENDS TO INCREASE CURRENT FLOW AND CORROSION. ALSO, AIR REACHING TOP OF PIPE TENDS TO DESTROY POLARIZATION WHICH OTHER-WISE WOULD TEND TO REDUCE CURRENT FLOW AND CORROSION.

CORROSION DUE TO IMPURITIES IN SURFACE OF PIPE
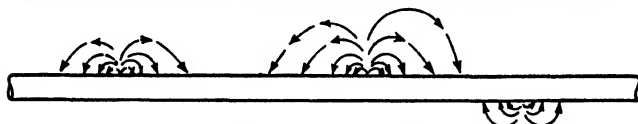
CORROSION CAUSED BY SMALL PARTICLES OR IMPURITIES IN SURFACE OF PIPE– IF THESE ARE ANODIC TO BALANCE OF SURFACE AND ARE SMALL IN AREA CONCENTRATED CORROSION OR PITTING RESULTS IN CORROSIVE SOILS.

CORROSION CAUSED BY DISSIMILAR SOILS

CORROSIVE SOIL

NON-CORROSIVE OR LESS CORROSIVE SOIL
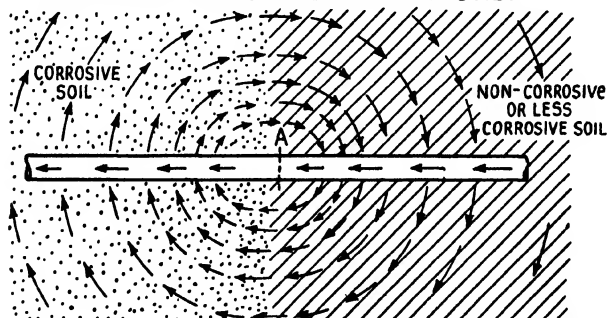
CORROSION IN AREA OF CORROSIVE SOIL IS INCREASED DUE TO PIPE EXTEND-ING INTO LESS CORROSIVE SOIL-INSULATING JOINT AT "A" MAY MATERIALLY REDUCE CORROSION

FIG. 28 (*Continued*)

of the soil in which they have lain, forming a crust of copper oxychlorides and oxycarbonates and tin oxide. A layer of copper oxide lies beneath this crust, often covering a core of metal. Sometimes the entire mass of bronze is converted to these compounds, leaving none of the original metal in the specimen. Fink and Eldridge found that the details of design in the original bronze were exactly reproduced in the layer of copper oxide which lies beneath the outer crust. Their fundamental idea was to replace cathodically the metal that had gone into the crust, since corrosion is generally conceded to be an electrolytic reaction. Experiments determined that the use of a 2 per cent solution of caustic soda as electrolyte was the safest for this purpose. The corroded object, without any preliminary cleaning, is hung in this bath as cathode, totally immersed. If the specimen be particularly soft as a result of attack, it is often necessary to wind it in several coils of fine annealed copper wire, or pack it in white sand. Anodes of iron, duriron, or platinum are hung on either side of the article. The container is generally a glass jar, although large tanks of heavy sheet iron or stoneware may be used, depending upon the size of the bronze. Low current densities are preferred. The evolution of hydrogen at the cathode will alter the crust to a powdered or spongy copper. When the gas is freely given off, the object is removed from the bath and washed by soaking several times in warm water. The film of reduced copper is brushed from the specimen, provided the latter were of hard metal under the corrosion crust, or is taken off by means of an acid dip if no core of metal be present. The exposed oxide surface, smooth and metallic, preserves all details of design.

Electrolysis by Stray Currents. Direct current is employed for many variable-speed mechanisms such as transit systems, elevators, transportation, and load-carrying devices. Power is usually supplied to these systems by overhead conductors such as "trolley wires" or by means of "third rails." Commonly the circuit is completed through the medium of the tracks or rails. These, however, particularly in wet weather, are not insulated from the ground, and earth circuits are possible. Metal pipes, cables, switching gear, etc., are possible parallel circuits for the return current. At the point of entrance of the current to these auxiliary conductors, the earth is anode and the metal pipe or cable cathode, but, where the current leaves to

continue in some other path, the pipe or cable is anode and electrolysis corrosion occurs. Of course, where the current leaves the rails, these will be subject to anodic corrosion. This type of stray-current electrolysis may be very destructive. With alternating currents of the usual frequencies (10 to 60 cycles) little if any difficulty is found.

Good rail bonds and rail beds of high resistance minimize this form of corrosion. Other methods involve insulated returns such as the "fourth rail," parallel buried conductors, or "pipe drainage" systems where the possible parallel conductors are made an integral part of the circuit.

The literature on corrosion, cathodic protection, and stray current electrolysis is extensive.[16]

GENERAL REFERENCES

Transactions of the National Association of Corrosion Engineers.
Corrosion Division of The Electrochemical Society.
"Corrosion Handbook," H. H. Uhlig, Editor-in-Chief, John Wiley & Sons, Inc., New York, 1948.

[16] MAGNUSSON, C. E., and SMITH, G. H., *Trans. Am. Inst. Elec. Engrs.*, **30**, 2055 (1911); BROWN, H. P., *Eng. News*, **65**, 684 (1911); ROSA, E. B., and McCOLLUM, B., Electrolysis and Its Mitigation, *Natl. Bur. Standards (U.S.) Technol. Paper* 52 (1915); McCOLLUM, B., and AHLBORN, G. H., Methods of Making Electrolysis Surveys, *Natl. Bur. Standards (U.S.) Technol. Paper* 28 (1916); Influence of Frequency of Alternating or Infrequently Reversed Current on Electrolytic Corrosion, *ibid.*, **72** (1916); LONGFIELD, C. M., *J. Inst. Elec. Engrs.*, **76**, 101(1935); LEWIS, K. G., and EVANS, U. R., *Korrosion Metallschutz*, **11**, 121 (1935).

CHAPTER 9

COLLOID ELECTROCHEMISTRY

When an electric current is passed through a porous diaphragm immersed in a liquid, the flowing of the liquid through the diaphragm is observed, the flow being commonly from the anode to the cathode, although it may take place in the opposite direction. It was first observed by Reuss[1] who used clay diaphragms in water and noticed that, as the current forced water through the clay toward the cathode, migration of suspended clay particles toward the anode occurred. The passage of a liquid through a diaphragm under the action of the electric current is termed "electrical endosmose" and the migration of particles in suspension "electrophoresis." Empirical electrokinetic relations were developed by Quinke, Wiedemann, and others. Helmholtz, and later Smoluchowski, derived theoretically the equation

$$U = \left(\frac{1}{90,000}\right)\frac{\zeta DX}{4\pi\eta} = \left(\frac{1}{90,000}\right)\frac{\zeta DI}{4\pi\eta L}$$

where U = electroosmotic velocity, cm per sec
  ζ = zeta (electrokinetic) potential, volts
  D = dielectric constant of the liquid
  η = viscosity of the liquid, poises
  L = conductivity of the liquid, mho-cm
  X = potential gradient, volts per cm
  I = current, amp

A similar equation holds for V, the electrophoretic velocity, with zeta equal to the potential of the particle. The historical aspects of this subject have been covered by Abramson[2] and

[1] Reuss, F., *Pogg.-Ann.*, **87**, 321 (1852); **99**, 177 (1856).

[2] Abramson, H., "Electrokinetic Phenomena," Chaps. I and II, Chemical Catalog Company, Inc., New York, 1934; Horowitz, W., The Theory of Electrokinetic Phenomena, *J. Chem. Education*, **16**, 519–534 (1939); Mueller, H., and Abramson, H., Electrophoresis, *Ann. N.Y. Acad. Sci.*, **39**, 105–212 (1939).

others. Wiedemann,[3] from a quantitative study of electrical endosmose, deduced threé empirical generalizations: (1) The mass of liquid transported in unit time through a porous diaphragm is directly proportional to the strength of the electric current, and, for a given diaphragm material and given current strength, it is independent of the length and sectional area of the diaphragm; (2) the difference in hydrostatic pressure maintained by electrical endosmose between the two sides of a porous diaphragm varies directly as the current strength and, for a given diaphragm material and a given current, is proportional directly to the length and inversely to the sectional area of the diaphragm; it is also proportional to the specific resistance of the liquid in the case of aqueous solution; (3) for a given diaphragm material, the difference in hydrostatic pressure maintained between the two sides of a porous diaphragm is proportional to the applied potential and is independent of the dimensions of the diaphragm. The action of the electric current on suspensions has been much studied in connection with colloid chemistry.[4]

Dehydration. The possibility of using electrical endosmose and cataphoresis in the removal of water from muds, pulps, and jellylike or spongy masses containing materials in suspension has been investigated in detail. Considerable study has been given to peat, which occurs in many places as a slimy material containing approximately 90 per cent of water. Filtration and centrifuging are not applicable because of the slimy nature of the peat pulp, which causes an impervious layer to form on the filter or in the centrifuge. Reduction of the moisture content of the peat from 90 to 50 per cent by evaporation requires 880 Btu. By air drying, the 50 per cent material can be converted into a product containing 20 per cent moisture and having a calorific value of 810 Btu per lb. One pound of the original peat mud produces less than $\frac{1}{8}$ lb of dried peat yielding not more than 1,000 Btu. Thermal methods for the removal of water are uneconomic. Schwerin[5] found that, if peat be placed between a

[3] Wiedemann, F., *Elektricität*, **1**, 1007 (1893).

[4] "Second Report on Colloid Chemistry and Its General and Industrial Applications," British Association for the Advancement of Science, London, pp. 26–52, 1921.

[5] Schwerin, B., *Z. Elektrochem.*, **9**, 739 (1903); *Ber. V. intern. Kongr. angew. Chem.*, **4**, 653 (1908).

wire gauze cathode and a plate anode, it is carried to the anode where it is deposited as a solid crust containing 50 to 60 per cent moisture. The potential gradient was 4 to 5 volts per cm, and 13 to 15 kwhr is required to remove 1 m³ of water. The process was a failure on a commercial scale because air drying of the material proved to be too tedious and costly. Electroosmotic processes can remove water only to the same extent as mechanical methods of separation and do not dry.[6]

Dewatering of Clay. The electroosmose process was applied to the dewatering and purification of clay for the purpose of transforming a low-grade and impure material into something approximating ball clay or china clay in quality. Clay mineral particles are charged negatively and deposit on the anode similarly to rubber latex particles. In a clay suspension, there is a heterogeneous mixture of charged carriers, including various ions and clay particles of all sizes. Deposition from such a system is necessarily a complicated phenomenon. In the older processes the impure clay is first made into a thin "slip" with water, the slip is allowed to stand until the coarser particles (usually silica) have had time to settle, and the fine particles of clay still remaining suspended in the slip are removed by gravity settling, filtration, or centrifugal separation. Schwerin proposed to hasten the process and improve the product by dewatering the suspended clay by electrophoresis. The clay slip was sent to a cell with a revolving metal drum anode, outside of which was a wire net cathode, surrounding the anode drum on the underside. The suspension was pumped between the electrodes, the impurities settled on or under the wire cathode, and the clay was deposited on the revolving drum anode. The voltage on the cell was 75 to 100, the anode current density under 0.1 amp per cm² (0.6 amp per sq in.). Energy consumption was 0.012 kwhr per lb of 35 per cent moisture material.

Speil and Thompson[7] studied the electrodialyzed and undialyzed clay to determine the yield per faraday, the energy consumption per ton of dry clay, and the moisture content of the deposit. The effects of temperature, time of deposition, current density, electrode spacing, solids concentration, conductivity,

[6] NERNST, W., *Verhandl. deut. physik. Ges.*, **11**, 112 (1909).

[7] SPEIL, SIDNEY, and THOMPSON, M. R., *Trans. Electrochem. Soc.*, **81**, 119–145 (1942).

type and amount of dispersant, and type of electrode were determined.

Bleininger[8] in 1915 used a rotating anode "osmose" machine for the purification of clays. No purification was obtained in the electrophoresis cell itself. Kohl[9] attributed the purity of the final clay product to the sedimentation of impurities prior to dewatering in the "electroosmose" machine. Hind[10] found no purification in electrophoretic dewatering. He gave data for a kaolin plant in Czechoslovakia as 78 kwhr per ton dry clay; 12.4 g per dm^2 per min; 35 per cent moisture in product; 42,000 g per F, while Prausnitz and Reitstötter[11] state that the energy consumption is 25 to 40 kwhr per metric ton of dry clay.

Speil[12] studied the electrical dewatering of a Tennessee ball clay. The conditions favorable to the process were close electrode spacing, high temperature, concentrated suspensions, moderate current density (approximately 1 amp per dm^2), long deposition time, until energy consumption per unit deposit became excessive. Ralston and Hoseh[13] electrodeposited a fine-grained Alabama kaolin. The moisture content of the deposit decreased with increased time of deposition and increased current density, and the yield per faraday was independent of current density. For the Alabama kaolin the apparent faraday equivalent was approximately 10,000 g per F under the conditions employed.

Electrical Tanning. Electrical tanning[14] of leather by bark extracts is the oldest practical application of electrical endosmose, having been originated, according to Buse, by Grosse in 1849. In 1874 de Meritens at Petrograd used electricity in 600 tan pits,

[8] BLEININGER, A. V., Use of Sodium Salts in the Purification of Clays, *Natl. Bur. Standards (U.S.) Technol. Paper* 51 (1915).

[9] KOHL, H., *Ber. deut. keram. Ges.*, **3**, 64–77 (1922).

[10] HIND, S. R., *Trans. Ceram. Soc.* (Brit.), **24**, 73 (1924).

[11] PRAUSNITZ, P. H., and REITSTÖTTER, J., "Electrophorese, Electroosmose and Electrodialyse," p. 170, T. Steinkopf, Dresden, 1931.

[12] SPEIL, SIDNEY, *Bull. Am. Ceram. Soc.*, **20**, 244 (1941).

[13] RALSTON, O. C., and HOSEH, M., *Trans. Electrochem. Soc.*, **80**, 85 (1941).

[14] FÖLSING, *Z. Elektrochem.*, **2**, 167 (1893); RIDEAL, S., and TROTTER, A. P., *J. Soc. Chem. Ind.*, **10**, 425 (1891); BUSE, J., *ibid.*, **19**, 57 (1900); RIDEAL, E. K., and EVANS, U. R., *ibid.*, **32**, 633 (1913); WILLIAMS, O. J., *J. Am. Leather Chem. Assoc.*, **8**, 398 (1913); GROTH, L. A., British Patent 19,239 (1912).

employing a layer of carbon at the bottom as anode, placing on this alternate layers of hides and tan bark, and concluding with a sheet of tin as cathode.   The electroosmotic method of tanning is decidedly more rapid than the ordinary diffusion process and would be a distinct success were it not for anodic oxidation of the tannin.   Schwerin has endeavored to prevent this by surrounding the electrodes with diaphragms.

Electrical "Lubrication."   An application of electrical endosmose is found in brick manufacture.   Wet clay has a tendency to adhere to smooth metal surfaces, and to prevent this, lubricants such as oils, emulsions, and water are used.   It was found that, if metal in contact with the clay be made cathode and a current be passed, the clay no longer tends to adhere and all the effects of lubrication are duplicated.   In making wire-cut bricks, electrical "lubrication" is said to reduce the power consumption by 25 to 30 per cent.   When the current flows, water is carried through the clay to the cathode (the metal) and forms a layer between it and the clay.   It is this layer of water which prevents the clay from sticking and acts as a lubricant.

Electrophoresis is applied in the manufacture of chemical stoneware to eliminate laminations.   These are caused by the drag of the forming dies on the surface films of the column of clay being expressed, which drag causes the inner sections of the body to slip on themselves and to travel at a slightly higher speed.   A fluid lubricating film is formed by the passage of an electric current through the clay while it is being shaped.   The die surfaces are made cathodes, and the anode is placed within the forming machine.   Small percentages of electrolytes are added to the clay during its preparation.   If the extrusion of a column of stiff clay be stopped for a short time with the current on, enough fluid material will be drawn to the die surface to make the outer section of the clay column slushy.   A reversal of the current will take away enough moisture to render the outer column of the clay bone dry and hard.   The direct current may be modulated by a pulsating current of fairly high frequency but so regulated that there is no polarity reversal.

Cataphoresis has been much studied by the colloid chemists.[15]

[15] "Fourth Report on Colloid Chemistry and Its General and Industrial Applications," British Association for the Advancement of Science, London, pp. 23–33, 1922.

Deposition of Rubber. Rubber latex behaves as a typical negatively charged colloid, coagulable by positive ions and, in an electric field, transportable toward the anode. Latex is the liquid obtained from the tapping of rubber trees, which upon coagulation yields raw rubber. Hauser[16] has given evidence that the latex particles behave as if they have an elastic, solid outer skin containing a viscous liquid. Cockerill[17] proposed to coagulate rubber electrically on a moving platinized belt anodically connected. Clignett[18] substituted electrical for acid coagulation at rubber plantations. The latex was contained in a long tank fitted with carbon electrodes in porous pots. Upon application of the current the rubber at first creams around the anodes. At this stage reversal of the current results in transference of the rubber to the other electrode. If, however, the current be not at first reversed, an increasing degree of coalescence follows the first stage of creaming, with subsequent formation of a solid layer of rubber at the anode. The process has been used practically for many years in Java. Sheppard[19] has shown that latex particles, when no current is applied, are in active Brownian movement, but under the field of a unidirectional current the particles move toward the anode, with reversal of movement if the polarity of the field be reversed. Under unidirectional electric fields, particles deposited on the anode build up multiparticle layers. Sheppard is of the opinion that there is a substantial identity in the processes involved in the electrical transport of matter in solutions, colloids, emulsions, and suspensions. Experimental evidence shows that electrophoresis and electroosmosis are inversely proportional to the actual conductivity of the solution. The movement of a true ion and the electrophoresis of a colloidal particle are each proportional to the potential gradient and likewise to the time. The velocity of electrophoric migration is a measure of the stability of the colloid or suspension. The actual behavior in the presence of electrolytes cannot be quantitatively predicted on any existing theory. Metals which are capable of anodic corrosion and form stable oxides compatible with the rubber deposit are preferred as anodes. With such

[16] HAUSER, E. A., *India-Rubber J.*, **69**, 663 (1925).
[17] COCKERILL, T., *India-Rubber J.*, **37**, 256, 331 (1909).
[18] CLIGNETT, H., "Rubber Recueil," p. 377, 1919.
[19] SHEPPARD, S. E., *Trans. Am. Electrochem. Soc.*, **52**, 52 (1927).

anodes, oxidative changes of the latex particles adjacent to the anodes are largely avoided. Zinc anodes have been found to be most useful, but copper anodes produce cuprous ions which lead to a very rapid breakdown of the rubber. Sulfur, fillers, pigments, and softeners in finely divided form can be added to the latex suspensions, and the mixed "compounds" can be electrically deposited uniformly and substantially in the proportions in the mix. The thickness which can be deposited is not necessarily limited, but from a practical viewpoint it is restricted by the question of drying and by secondary changes in the surface layers. Rubber produced by electrodeposition may be readily vulcanized. It also permits the use of so-called "superaccelerators," which cannot be used in milled stock because they act so rapidly that scorching results. The tensile strength of electrodeposited rubber is exceptionally high. Salts and hygroscopic bodies are readily washed out upon completion of electrodeposition, resulting in a product of high insulating properties.

With large particles the current efficiency of deposition of rubber is very high. A comparison with the electrodeposition of metals shows that at a current density of 10 amp per sq ft (1.08 amp per dm^2) approximately 2.5 hr would be required to deposit 1 oz of nickel per square foot (30.5 g per dm^2), while, taking the low value of 2,000 g per F, this weight of 50 per cent rubber could be deposited, at 80 amp per sq ft (8.6 amp per dm^2) in 17 sec; at the same current density 68 times as much rubber could be deposited in that time as nickel. At the higher concentrations of rubber (upward of 25 per cent) the comparison is still more striking, the amount of rubber being deposited becoming 100 to 300 times the amount, say, of zinc for the same current. Some factors of composition, current efficiency, and power requirements are shown in Table 22.

The throwing power in the electrodeposition of rubber is not very high, owing to the low conductivity, but is apparently higher than would be expected considering this factor. It is generally sufficient to take care of recessed angles, edges, and bends. The factors in throwing power of rubber latex baths probably differ in some respects from those in metal-plating solutions and are under investigation.

In commercial application metallic anodes are coated with porous materials, for example with a fabric or with gelatin, or surrounded at a distance by a porous diaphragm, and the rubber

latex including compounded dispersions is electrolyzed, with the resultant deposit of rubber upon the membrane or diaphragm.[20] Commercial conditions for thicknesses of rubber of $\frac{1}{32}$ to $\frac{1}{8}$ in. are given in Table 23. Voltages range from 10 to 100, depending upon the current density, size and shape of the article plated, the diaphragm resistances, and related factors. The flow sheet

TABLE 22. CURRENT EFFICIENCY OF RUBBER DEPOSITION

Bath	Rubber, g per 100 cc	Sulfur, g per 100 cc	Zinc oxide, g per 100 cc	Ammonia, g per 100 cc	Conductance ratio per cc $\times 10^{-3}$	Rubber compound per faraday, g	Kwhr per lb at 50 volts
A ...	7.00	0.00	0.0	0 150	3 22	1,490	0 408
B....	7.00	0.14	0.0	0 150	3 16	1,390	0 381
C... .	7.00	0.00	7.0	0 150	3 27	2,000	0.304

NOTE.—In bath A no zinc oxide was introduced, but the rubber plating contained 3.15 per cent, owing to the electrolytic oxidation of the zinc anode. In bath B, the rubber-sulfur ratio in the liquid was 98:2, in the solid deposit 95:2, a difference attributable to loss of soluble rubber constituents on electrodeposition. In bath C, ratio rubber to zinc oxide was 100:100, in the solid 100:101.

Higher values of the deposition per faraday and the current efficiency are obtained with lowered conductivity and increased rubber content.

TABLE 23. RUBBER DEPOSITION

Electrolyte:
  Anolyte:
    Rubber and compounding ingredients, %   35
    Ammonia, g/l   20
    Alkali metal and ammonium salts, g/l.   30
    Specific conductivity, mhos/cc......   (3 to 8) $\times 10^{-3}$
  Catholyte ....   Water with pH greater than 7

Anode c.d., amp/sq ft   . .   .   7–22
Voltage......   10–100
Anode deposit:
  Per cent solids.   60
  Per cent H_2O..   40
Anode material.. .   ...   Zinc or zinc-plated iron

Deposition rate:
  Grams/amp-min................................ 1.2–1.5
  Grams/F...................................... 1,900–2,400

[20] See SHEPPARD, S. E., and EBERLIN, L. W., U.S. Patent 1,476,374; and KLEIN, P., British Patent 223,189; KLEIN, P., U.S. Patent 1,548,689; SHEPPARD, S. E., and BEAL, C. L., U.S. Patent 1,589,325; KLEIN, P., and SZEGVARI, A., U.S. Patent 1,825,736; BEAL, C. L., *Ind. Eng. Chem.*, **25**, 609 (1933). The process was independently invented and developed, in 1921 and 1922,

of the process and a diagrammatic cross section of the cell are given in Fig. 29.

Bitumen Deposition. Electrodeposition of materials like bituminous emulsions[21] is employed for the protection of underground pipe lines or the restoration of the same after they are mechanically cleaned. The pipe is filled with the bituminous emulsion, and a central wire in the pipe serves as the cathode while the pipe itself is the anode. The deposition voltage is adjusted as a function of the desired thickness of coating. The bitumen or asphalt is deposited out of the water emulsion at the anode which is the inside surface of the pipe. As the coating builds up, its resistance increases, and at constant voltage the current flow through the circuit decreases, so that finally it becomes zero. Another section of the pipe is then coated by drawing the cathode forward a distance equal to its length and the operation repeated. Inasmuch as the bitumen is electroplated out of an aqueous dispersion, the pipe is coated despite the fact that its surfaces are wet. It would not be possible to coat a wet pipe with ordinary paints.

Resin Deposition. Gemant[22] used hydrophobic insulating liquids, chiefly mineral oils, as the dispersing phase for suspensions of synthetic resins, from which suspensions electrodeposition of the resins was effected. Gemant found that the rate of deposition increases linearly with voltage, as predicted by the Helmholtz equation, but only up to a critical voltage, above which a phenomenon called "dielectric displacement" occurs. The liquid phase, with higher dielectric constant, tends to concentrate at the surface of the wire to be coated, the point of highest field density.

Feinleib[23] studied the electrolysis of suspensions at lower voltages than those of Gemant. Applications are possible in the fields of corrosion protection of metals, electric insulation, and in the production of thin plastic sheets or thin-walled plastic articles of any desired shape or design.

---

by S. E. Sheppard and L. W. Eberlin of the Eastman Kodak Company in the United States, and by P. Klein of Budapest, Hungary, together with Szegvari and other associates.

[21] DANN, G. H., *Water Works Eng.*, **101**, 44, 70 (1948).

[22] GEMANT, ANDREW, *J. Phys. Chem.*, **43**, 743 (1939); *Ind. Eng. Chem.*, **31**, 1233 (1939).

[23] FEINLEIB, MORRIS, *Trans. Electrochem. Soc.*, **88**, 11–23 (1945).

A—Anode with deposit of latex rubber
B—Cathodes
B_1—Cathode diaphragm
B_2—Cathode compartment
C—Latex mix
D—Deposited rubber
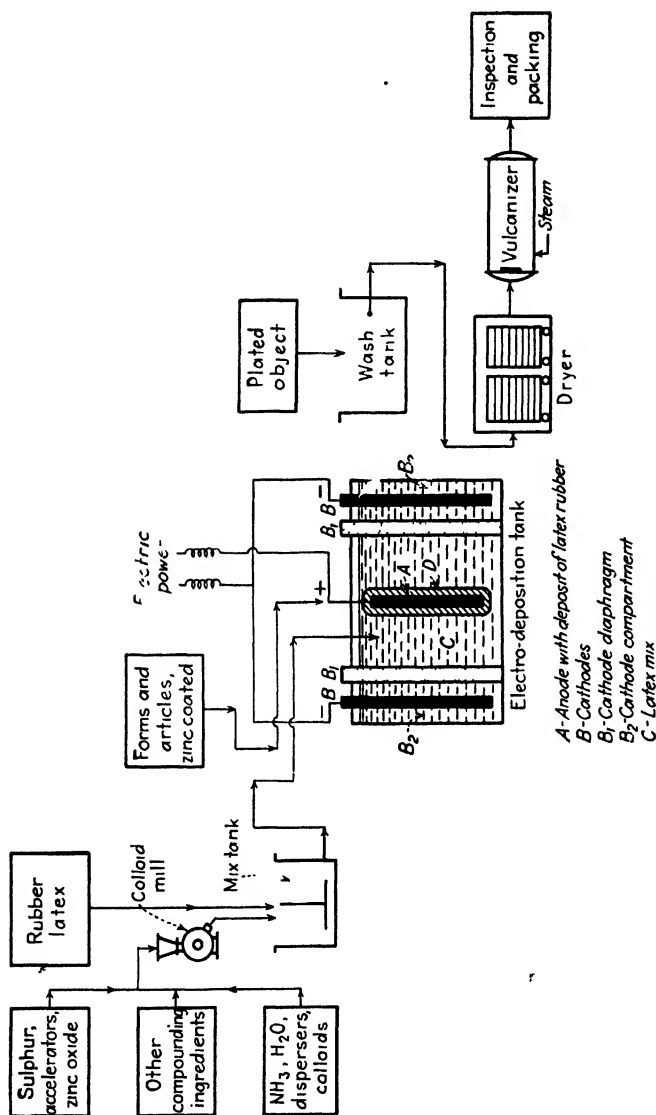
Fig. 29.   Anode process of rubber deposition.

CHAPTER 10

PRIMARY CELLS

That section of electrochemical engineering which concerns itself with the conversion of chemical into electrical energy is much less important than the inverse operation in which substances are produced by means of the electric current. This statement would be incorrect were it possible to convert the chemical energy obtained by the combustion of fuels directly into electrical energy. The conversion of chemical into electrical energy is a function of primary cells or batteries. The latter term is loosely used for designating a single unit but is properly applied to an assembly of identical units or cells. These are employed for the intermittent production of small amounts of electrical energy. They are largely used for electrotherapeutic purposes, electric bells, signal systems, lighthouse control, very small motors intermittently used for control purposes, small private telephone systems, motor ignition, while more efficient and larger forms can be employed for isolated installations of electric lighting and the driving of small motors and lathes. The high cost of primary cells and batteries makes the production of electricity from them in large quantities impractical.

Before and during the Second World War there developed an urgent need for special-purpose batteries of high capacity (with the disadvantage of short life), high voltage, light weight, and other characteristics for radio sond, guided missiles, pilot balloon lights, electronic controls, control radio operation, and the like, as well as short-time operation of special motors, mechanisms, and devices. Large quantities of magnesium-silver chloride cells were manufactured in a wide range of sizes, capacities, and voltages.

The emf of a primary cell resulting from the combination of two electrode systems, one with a high positive or oxidizing and the other with a strongly negative or reducing potential, can be determined from the table of single potentials. The emf of

160

such a cell is then the difference between the two potentials. Theoretically, numerous systems may be established; the majority of them, however, will be found impracticable on various accounts such as costliness, chemical activity of the anode material, or tendency to passivity. In practice zinc is used almost invariably as the soluble anode in a primary cell.

Assuming that the electrode system and its resulting reactions are reversible, the emf of the cell may be calculated from the Gibbs-Helmholtz equation. The theoretical emf may be determined from the heats of reaction of the cell materials. In practice, however, electrode systems never behave absolutely reversibly. Passivity is avoided by the use of soluble anode materials and controlled electrolytes, with emphasis given to constituents which are anode corroding agents. The terms "anode" and "cathode" are employed here with reference to the inside of the cell. When current is drawn from the cell and the unit serves as an energy source, it follows that the positive terminal is the projection of the cathode, and the negative terminal is the projection of the anode. At the cathode in simple cells there is a reversible discharge of metallic ion to metal. In others, as the Lalande or the Leclanché, an indifferent electrode surrounded by a depolarizing oxidizing agent may constitute the cathode at which H^+ ions are discharged. The depolarizers increase the emf of a cell above the normal reversible H^+ ion discharge. The electrode does not become saturated with hydrogen owing to the speed of the reaction between the depolarizer and the hydrogen.

A satisfactory depolarizer must be a good conductor and make effective contact with the electrode as well as react rapidly with the hydrogen. In older types of cells liquid depolarizers were used. They had the advantage of rapid reaction, but the disadvantage of diffusion toward, and of attack on, the anode. Diaphragms were often necessary and the cell resistance was increased. The more effective the depolarizers, the more closely will the cell system approach the equilibrium or theoretical value.

Before the expansion of electrical transmission lines and extensive distribution systems, a large number of different primary batteries were marketed. Some of these are employed, to any extent, only in laboratory work, military activities, army field-communication systems, or in isolated telephone exchanges.

The list includes the Daniell cell, the Grove-Bunsen, the bichromate or chromic acid cell, the Lalande caustic cell, and the Leclanché, the most common type of which is the widely known dry cell.   The last is the most important, followed by the Lalande. The use of the bichromate cell is decreasing.   The individual cells and their modifications will be briefly discussed.   The cell systems with their name designations, reactions, and open-circuit emfs are given in Table 24.

Daniell Cell.   The Daniell cell consists of the system $Zn|$ $ZnSO_4|CuSO_4|Cu$,

$$Zn + CuSO_4 = ZnSO_4 + Cu$$
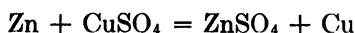
whose voltage is given approximately by the formula

$$E = 1.1 + 0.029 \log \frac{(Cu^{++})}{(Zn^{++})} \text{ volts}$$

where the ionic ratio is that of the molar Cu^{++} concentration of the catholyte to the molar Zn^{++} concentration in the anolyte. If there be little difference in the concentrations of the copper and zinc sulfates, the ionic ratio can be replaced by the calculated ratio of the two salts whose ionizations are quite similar under similar conditions.   The emf of the cell is practically independent of temperature.   The sign of the temperature coefficient is a function of the concentration of the electrolytes, becoming more positive with increase of the ratio Cu^{++}/Zn^{++}.

The commercial form of the Daniell cell consists of a glass jar or container which holds an inner porous cup.   The latter is surrounded by a saturated solution of $CuSO_4$ containing excess crystals and further by the cathode of copper foil bent to a cylindrical form.   The inner pot contains $ZnSO_4$ solution acidified with H_2SO_4 into which dips the zinc anode rod, generally of amalgamated metal.   The cell emf is a function of the concentration of the $ZnSO_4$ solution, having a maximum value of about 1.14 volts.   Without the addition of H_2SO_4 the voltage becomes 1.07.   The setup is not adapted to stand on open circuit, since the chemical reactions between the constituents continue whether the cell be in use or not.   When withdrawn from service, the unit should be emptied of all liquid, and the porous cup thoroughly cleaned, to avoid any cracking which might result from the expansion of the salts in its pores on drying.

TABLE 24. PRIMARY BATTERIES

Type	System	Emf	Reaction	Internal resistance, ohms
Bunsen..........	$HgZn$|1 part H_2SO_4 + 12 parts H_2O|conc. HNO_3|C	1 94	$Zn + H_2SO_4 + 2HNO_3 =$ $ZnSO_4 + 2H_2O + 2NO_2$	0 1–0.2
Bichromate or Poggendorf	$HgZn$|1 part H_2SO_4 + 12 parts H_2O|conc. -oln. $Na_2Cr_2O_7 + H_2SO_4$|C	2 00	$3Zn + 2H_2CrO_4 + 6H_2SO_4 =$ $Cr_2(SO_4)_3 + 3ZnSO_4 + 8H_2O$	0 2–0.5
Daniell or gravity	$HgZn$|5% soln. $ZnSO_4 \cdot 6H_2O$|sat. soln. $CuSO_4 \cdot 5H_2O$|Cu	1 07	$Zn + CuSO_4 = ZnSO_4 + Cu$	
Féry	Zn|12% NH_4Cl soln.|depolarizing C	1 2	$Zn + 2NH_4Cl = Zn(NH_3)_2Cl_2 + H_2$ $2H_2 + O_2 = 2H_2O$	
Grove	$HgZn$|1 part H_2SO_4 + 12 parts H_2O|fuming HNO_3|Pt	1 96	$Zn + H_2SO_4 + 2HNO_3 =$ $ZnSO_4 + 2H_2O + 2NO_2$	0 1–0.2
Leclanché	$HgZn$|20% NH_4Cl soln.—MnO_2|C	1 5	$Zn + 2NH_4Cl + 2MnO_2 =$ $Zn(NH_3)_2Cl_2 + H_2O + Mn_2O_3$	
Lalande	Zn|18–19% $NaOH$ soln.—oxides of Cu|Cu	0 95	$Zn + 2NaOH + CuO =$ $Na_2ZnO_2 + H_2O + Cu$	
Dry cell	Zn|NH_4Cl–$ZnCl_2$—MnO_2|C	53	$Zn + 2NH_4Cl + 2MnO_2 =$ $Zn(NH_3)_2Cl_2 + H_2O + Mn_2O_3$	
Le Carbone	Zn|20% $NaOH$|special C	: 4	$Zn + 2NaOH = Na_2ZnO_2 + H_2$ $2H_2 + O_2 = 2H_2O$	
Air cell	Zn|soln. $NaOH$|special C	1 25	$Zn + 2NaOH = Na_2ZnO_2 + H_2$ $2H_2 + O_2 = 2H_2O$	
Silver chloride	Zn|NH_4Cl—$AgCl$|Ag	1 0	$Zn + 2NH_4Cl = Zn(NH_3)_2Cl_2 + H_2$ $H_2 + 2AgCl = 2HCl + 2Ag$	
Magnesium-silver chloride	Mg|tap H_2O $AgCl$|Ag	1 6	$Mg + 2HOH \rightarrow Mg(OH)_2 + H_2$ $H_2 + 2AgCl = 2HCl + 2Ag$	
Silver oxide-zinc-alkali	Zn|KOH|Ag_2O_2	1 9	$2Zn + 2KOH + Ag_2O_2 =$ $2Ag + 2KHZnO_2$	
Lead-perchloric acid	Pb|$HClO_4$|PbO_2	2 06	$PbO_2 + Pb + 2HClO_4 =$ $Pb(ClO_4)_2 + H_2O$	
R.M	Zn|$Zn(OH)_2$ solid—KOH aq.—HgO solid |Hg	1 34	$Zn + H_2O + HgO \rightarrow Zn(OH)_2 + Hg$ $\uparrow\downarrow$ $ZnO + H_2O$	

The *gravity cell* shown in Fig. 30 is a modification of the Daniell cell which dispenses with the porous diaphragm. The $CuSO_4$ solution is placed in the bottom of the glass container, in contact with a copper-sheet electrode to which a rubber-covered wire connection is made. The $ZnSO_4$ solution is carefully poured on top of the catholyte and the sharp dividing line, indicated by the differences in color, is maintained when a small current is flowing. The zinc electrode, often in the form of a cast crowfoot, is suspended at the top of the jar. A coating of paraffin is generally applied on the edges of the jar to prevent creepage of the $ZnSO_4$ crystals over the top. In use, a thin layer of mineral oil over the top of the solution serves to reduce evaporation. Like the Daniell, this type of cell is unsuited for open-circuit work, inasmuch as the copper would tend to diffuse upward and precipitate on the zinc. It has many obvious disadvantages, including the unavoidable local action which occurs in various parts of the unit. Only about 30 per cent of the zinc is electrochemically utilized under average conditions.
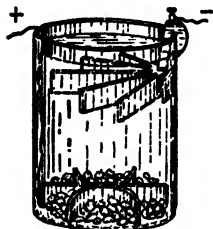
FIG. 30. Gravity cell.

Grove-Bunsen Cell. The Grove-Bunsen cell has the system amalgamated $Zn|$dilute $H_2SO_4|$strong $HNO_3|$Pt or C. Grove used a platinum cathode for which Bunsen substituted carbon. The anode consists of amalgamated zinc, usually in 8 per cent H_2SO_4. The construction is quite similar to that of the Daniell cell, but with the catholyte and cathode inside the porous cup, the zinc anode and the H_2SO_4 in the outer container. During operation objectionable fumes of the oxides of nitrogen are liberated. The cathodic process is a function of the concentration of the HNO_3. Pure aqueous HNO_3, whether strong or dilute, is not a reversible depolarizer, but the nitrous acid formed by the reaction with hydrogen aids depolarization. Large currents can be taken from the cell without serious drop of voltage, so that the unit is adapted to laboratory purposes where heavy currents are needed having more or less constant potential. The unit must not be permitted to stand on open circuit, but must be freshly made up for each use.

Bichromate Cell. The bichromate or chromic acid cell of Poggendorf has the system $Zn|H_2CrO_4|C$, using no diaphragm

and but a single solution.   Either H_2CrO_4, or sodium or potassium bichromate with H_2SO_4 may be employed to form the H_2CrO_4 solution.   The *Grenet* plunger type (Fig. 31) shows the arrangement of the two carbon plates and the zinc plate which can be lifted out of the cell when not in use.   The *Fuller* modification, employed in telephone practice on small isolated exchanges, uses a porous porcelain cup between the carbon and zinc electrodes.   An average electrolyte would contain 17 to 20 parts $Na_2Cr_2O_7$, 20 to 24 parts H_2SO_4, and 100 parts of water.

Lalande Cell.   The Lalande type of battery is generally known at the present time as the "caustic soda primary battery," the name being derived from the nature of the electrolyte, a solution of caustic soda. Amalgamated zinc forms the anode and cupric oxide the cathode and depolarizer. As in the gravity battery, a thin layer of oil on the surface of the electrolyte prevents its evaporation

FIG. 31.   Grenet plunger cell.

and the formation of carbonate.   The copper oxide and zinc electrodes with insulators are arranged so that the entire assembly may be secured to a cover, usually of porcelain, by a single suspension bolt and the necessary nuts and washers.   The terminal wire from the zinc is a copper wire with insulation of a rubber compound.

More than 90 per cent of all the batteries of this type are used for railroad signals and other railroad devices.   The units are of sufficient capacity to contain 4,400 cc of water in which the NaOH is dissolved.   The system is Zn|alkali solution|oxides of copper—Cu.   A typical cell is shown in Fig. 32.   The containing jar is made of a special glass to withstand the strong corrosive action of the caustic soda electrolyte for the duration of its service.   It must be proof against cracking owing to the heat generated in dissolving the caustic soda.   The electrolyte is usually 18 to 19 per cent NaOH.   The CuO, which functions as cathode and depolarizer, is made in a compressed or in a loose form.   For the compressed form, which is more generally used, the CuO is ground to a fine powder, mixed with a suitable binder, and subjected to heavy pressure.   It is then baked and the outer

Fɪɢ. 32. (a) Lalánde cell. (b) Exhausted Lalande cell. (*The Waterbury Battery Company.*)

surface metallized by partial reduction to increase the conductivity of the electrode, CuO in itself being a very poor conductor. The container for the loose oxide, as well as the finished form of the compressed oxide, generally takes the shape of a flat plate or hollow cylinder. The zinc electrode is cast in a cylindrical form and amalgamated with mercury either in the casting or by dipping in a mercury bath, the mercury content of the electrode being about 2.5 per cent. Purity of materials is important for the successful operation of the cell. The *Edison* modification of the Lalande cell uses flat plate electrodes, the zinc plates being cast with ribs. The compressed copper oxide electrode is suspended centrally with zinc on each side.

The chemical reaction of the unit may be represented by the equation

$$Zn + 2NaOH + CuO = Na_2ZnO_2 + H_2O + Cu$$
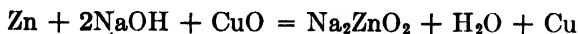
The emf is approximately 0.95 volt; but when heavy currents

are furnished, the terminal voltage is lowered to less than two-thirds of this value. The internal resistance of the cell is low. During operation the CuO electrode is gradually reduced to copper. Therefore upon exhaustion of the cell this electrode must be washed and reoxidized by heating at 150°C, and at the same time fresh zinc plates must be added to the unit. Commercial batteries are manufactured in sizes varying from 75 amp-hr up to cells with a rated capacity of 1,000 amp-hr. They are simple in construction, work readily, and are relatively cheap. For these reasons, and in spite of their low voltage, these cells have found extensive application in the operation of signal systems and other railway work. Seven unit electrode systems in a single container are now made for batteries which maintain their voltages from 500 to 1,000 amp-hr.[1]

Leclanché Cell. The Leclanché cell has the system $Zn|NH_4Cl$-$MnO_2|C$. In the original form the carbon rod was contained in a porous cup filled with crushed carbon and MnO_2. The mixture of these two was carefully made and pressed to obtain intimate contact. In later forms the MnO_2 and carbon were molded together into a cylindrical form by the use of a binder, the zinc electrode being suspended centrally. The electrolyte is a strong NH_4Cl solution, usually about 20 per cent. The open-circuit emf of the cell is about 1.5 volts, but when heavy currents are drawn from the cell, the terminal voltage drops rapidly to 1.1 to 1.2 volts. It is suitable for work on open circuits, but on closed circuits it is suitable only if large currents be drawn intermittently for short periods.

Silver Chloride Cell. The AgCl cell, which is similar to the Leclanché save that AgCl is used as a depolarizer with a silver electrode, is made in small sizes for use in army maneuvers and field service. The life of this cell is rather long for the size, and the open-circuit voltage is 1 volt. With magnesium substituted for zinc, the system became the basis for cells widely used in the Second World War.

Féry Cell.[2] For use where only low currents are required, as in some forms of railway work, the Féry cell was developed to avoid cathodic depolarizers completely. It is a modification of

---

[1] Martus, M. L., *Trans. Electrochem. Soc.*, **68**, 151 (1935).

[2] Féry, C., *Congr. intern. élec.*, Paris, Sec. **7**, *Rapport* 14 (1932); *Science Abstracts*, **35B**, 701.

the Leclanché in which air dissolved in the carbon is employed for depolarizing the hydrogen discharge. In the French railway type a zinc plate electrode rests at the bottom of a glass jar containing the electrolyte, which is 12 per cent NH_4Cl. The carbon electrode, in the form of a hollow carbon cylinder, is arranged vertically and carried on a cross-shaped insulator of synthetic plastic or ebonite. The carbon electrode is pierced with holes and is about half the diameter of the jar, projecting several inches above the top of the electrolyte which surrounds most of its surface. Oxygen for depolarization is adsorbed from the atmosphere by the carbon. Cells show a life of about 6 months at discharge currents of 20 to 50 milliamp. They have an open-circuit voltage of 1.2 and a 90-amp-hr capacity for a cell weighing 2.1 kg.

Superior forms of air-depolarized cells have been commercially developed using activated carbon cathodes and an electrolyte of 20 per cent sodium hydroxide.

Air Cells. The air-depolarized cell comprises a caustic alkali electrolyte, an anode of amalgamated zinc, and a carbon cathode capable of utilizing atmospheric oxygen. The operating voltage is of the order of 1.1 to 1.2 for ordinary loads, and the open-circuit voltage of a fresh cell 1.4 to 1.45. The cathode is of nongraphitic carbon with powdered charcoal as one of the principal constituents, manufactured in such a manner as to be sufficiently porous and gas permeable to "breathe air" and yet close-grained enough to resist electrolyte penetration. Heise and Schumacher[3] state that the carbon has an apparent density of 0.6 to 0.8, a porosity of 50 to 65 per cent, a resistivity of 0.0075 to 0.015 ohm per cm^3, and a gas permeability of 100 to 1,000 cc of air per cubic centimeter per minute. Oxide complexes at the electrode interface are considered to be the depolarizer. The electrode is waterproofed with paraffin. The electrolyte is usually a 20 per cent $NaOH$ solution, which composition is satisfactory for low-temperature service. Lime is added to the electrolyte to slowly react with the sodium zincate formed as the result of solution of the zinc anode, with the regeneration of caustic.[4]

    [3] HEISE, G. W., and SCHUMACHER, E. A., *Trans. Electrochem. Soc.*, **62**, 383 (1932).
    [4] U.S. Patents 1,835,867 (Dec. 8, 1931), 1,864,652 (June 28, 1932).

Figure 33 shows a two-cell unit made for operation of 2-volt radio tubes. These batteries are stated to be good for about a
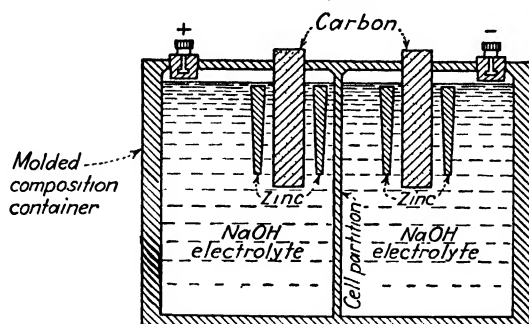
Fig. 33. Air cell—two cell battery.

year of service when operated 3 'r a day. The voltage characteristics of the air cell are given in Fig. 34.

In its commercial form the cell is shipped dry with the necessary caustic in cast form around the anode and cathode and with lime in dry form at the bottom of the container. The cell is "activated" by the addition of water to the electrolyte level.

Primary batteries of the adsorbent-carbon depolarizing type are
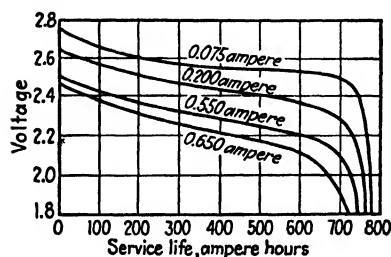
Fig. 34. Voltage characteristics of an air cell.
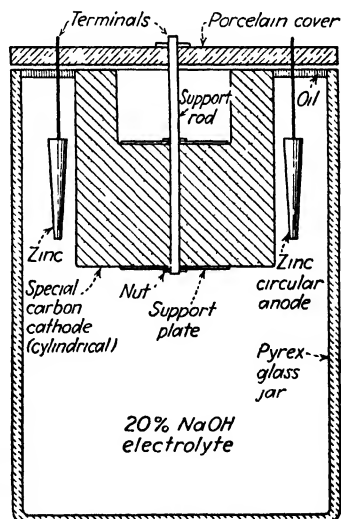
Fig. 35. Le Carbone caustic cell.

also built for semaphore, highway flashing systems, lighthouses, railway signals, and similar work. A typical one is the Le Carbone cell, the construction of which is shown in Fig. 35 and the

characteristics in Fig. 36. A cell whose cylindrical glass jar is approximately 10 in. high and 7 in. in diameter is rated at 500 amp-hr, with initial closed-circuit voltage of over 1 volt at rates of discharge not greater than 3 amp. The positive or carbon element has a capacity of 2,000 to 2,500 amp-hr, while the zinc circular element, weighing about 825 g, lasts 500 amp-hr, after which it is renewed. The cell holds about 4 liters of a 20 per cent
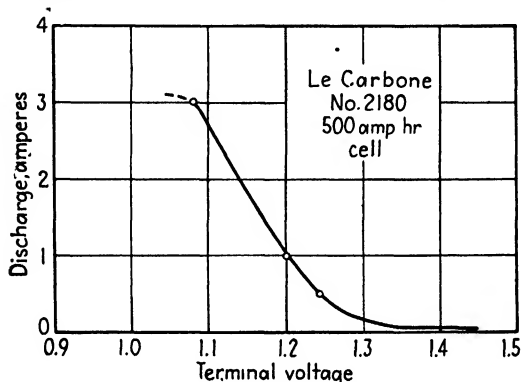
FIG. 36.   Current-voltage relations of Le Carbone cell.

NaOH electrolyte, which is renewed every 500 amp-hr. The open-circuit voltage of the cell is 1.4 to 1.5 volts.

Dry Cells. The dry cell is the outgrowth of the Leclanché cell. Leclanché expressed the voltage of his cell in terms of the $CuSO_4$ cell, and its external resistance in terms of meters of iron wire of a certain diameter. He refers to the depolarizing action of the MnO_2 as combustion of hydrogen. The success of the Leclanché cell led to numerous attempts to make its electrolyte unspillable. Various absorbents and fillers, including sand, sawdust, cellulose, asbestos fiber, plaster of paris, spun glass, were tried out during the 20 years following. In 1888 the first successful dry cell was produced by Gassner.[5] It consisted of a zinc can serving as anode and as the cell container, a carbon rod surrounded by the depolarizing mixture which was wrapped in cloth, and the electrolyte in the form of a jelly. Its voltage on open circuit was about 1.3 volts, and its short-circuit current about 6 amp. The

[5] COOPER, W. R., "Primary Batteries," p. 3, Benn Brothers, Ltd., London, 1917; AYRTON, W. E., and MATHER, T., "Practical Electricity," p. 192, 1912; *Natl. Bur. Standards* (*U.S.*), *Circ.* 79.

dry cells of the present day have been developed from this cell of Gassner.

The dry cell has been so designated because its electrolyte is contained in an absorbent material which prevents its spilling out regardless of the position of the cell. The cell is not dry, however. In fact, one of the essential requirements in its make-up is that it be sufficiently wet under all ordinary conditions.

The reaction of the Leclanché and the dry cells may be given as

$$Zn + 2NH_4Cl + 2MnO_2 = Zn(NH_3)_2Cl_2 + H_2O + Mn_2O_3$$
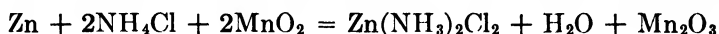
It is thought that the depolarization action of the MnO_2 results in the oxidation of the hydrogen to water and the formation of the lower state of oxidation of the manganese, probably Mn_2O_3.

Ordinarily the zinc serves as a container for the cell. The electrolyte is an aqueous solution of NH_4Cl and $ZnCl_2$. It is held partly in an absorbent material and partly in the mixture of ground carbon and MnO_2. The lining separating the zinc and the depolarizing mixture must allow electrolytic but not metallic conduction, in that the latter would cause the formation of an internal short circuit. The depolarizing mixture is bulky and occupies most of the interior of the cell. The electrolyte is sometimes made into a jelly with colloidal materials such as gum tragacanth, agar-agar, gelatin, flour, or starch. The electrolyte, therefore, will not spill, whether it be completely sealed over at the top, the method most common in American practice, or provided with a vent for the escape of gas, which is the European custom.

When the cell is new, the surface of the composite carbon-MnO_2 electrode may be taken as the outside surface of this mixture next to the zinc. As the cell is discharged, the MnO_2 is reduced, and the effective surface of the electrode moves toward the carbon rod, which is in the center axially with the cell. This carbon rod only serves to conduct the current out of the mixture to the terminal.

Two general sizes of dry cells are manufactured: a large one for ignition, signaling, and miscellaneous intermittent use, and a smaller size for flashlights, radio batteries, and similar purposes. In the larger size sheet zinc is used as the container, the bottom being soldered with lap seams, while zinc stampings are employed for the smaller cells. It is essential for electrochemical reasons, to

avoid galvanic couples and local corrosion of the metal, that the zinc be of a high degree of purity. It must at the same time have high tensile strength and elongation as well as stiffness, in order to withstand manufacturing operations.

The electrical conductivity of the MnO_2 depolarizer is very low so that granulated carbon, more or less completely graphitized, or acetylene black is added to increase the conductivity of the mixture. Regarding the NH_4Cl electrolyte, it is desirable that it be free of metals such as Cu, Pb, Fe, As, Ni, Co, and Sb which may be plated out by the zinc, as well as free from negative radicals, such as sulfates, which form compounds less soluble than the chlorides. Insulation and sealing compounds are usually resin, sealing wax, or bituminous pitches with fillers such as ground silica, fibrous talc, and coloring matter added. The entire cell is ordinarily insulated by a strawboard container or jacket surrounding it.

The MnO_2 used in dry cells is a refined ore, or an MnO_2 produced by anodic oxidation. Its efficiency in this particular use depends upon the percentage of MnO_2 and probably its state of hydration. The ore employed almost exclusively is pyrolusite. Its value as an oxidizer in dry cells varies with the content of the dioxide and its crystalline state as indicated by X-ray examination. The ore must be free from copper, nickel, or cobalt, as small traces of these metals may destroy the cell. Iron to the extent of 1 per cent is not unusual, and it has been shown by manufacturers of dry cells that even 2 to 3 per cent in some cases may be allowed. Iron in the metallic or ferrous condition is the most harmful.

The physical qualities of fineness and porosity are of great importance. In general, it appears that an increase in the size of the grains up to a certain limit reduces the internal resistance of the carbon-MnO_2 mixture, while a decrease in size of the grains increases the depolarizing power per unit weight of MnO_2. A high degree of porosity is desirable inasmuch as the depolarizing power depends upon the surface area of the MnO_2.

Two general methods of manufacture are employed, the most familiar one for larger cells in the United States being the paper-lined method. The zinc container is lined with a sulfite and ground wood-pulp board at the sides and bottom, into which the MnO_2-NH_4Cl-$ZnCl_2$ mixture is tamped around the central carbon

electrode. The pulp board lining is then folded down over the top of the mixture and the cell sealed with a sealing compound. The construction of a typical cell is shown in Fig. 37.

The second method is termed the "bag" or "sack" type, in which the carbon rod with its surrounding mixture of electrolyte and depolarizer is wrapped in muslin and tied with a string, forming a unit which is placed in the zinc can, leaving sufficient space between the two for the electrolyte. The construction is shown in Fig. 38. The solution of sal ammoniac and $ZnCl_2$ is thickened with flour or other gelatinous materials. Spacers to
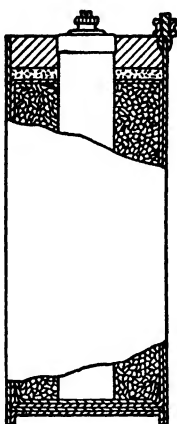
Fig. 37. Section of paper-lined cell.   Fig. 38. Section of bag-type cell.
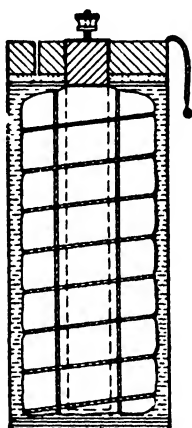
separate the bag from the zinc can are desirable but are not always used. This form of construction is almost universally used for making small flashlight batteries. It tends to increase the life of the small cells, which may be shorter than that of the larger sizes even when standing on open circuit. Some of these units are so small that most of the operations can be done by hand more readily than by machinery.

A modification of both these forms of construction is the desiccated cell which is manufactured dry and requires the addition of water before it is ready for use. The water is introduced through an opening provided in the seal or center of the carbon rod. Some cells are also provided with a vent.

Since dry cells of the smaller sizes are subject to deterioration during the time of standing on the dealers' shelves, an effort has

been made by several of the manufacturing companies to furnish partially assembled cells that are freed from local action by a separation of one or both of the electrodes from the electrolytic paste. Such cells are arranged for quick and simple assembly by the purchaser.

Daniels[6] has calculated that the energy of an 85-g D cell is equal to almost 13,000 watt-sec. Such a unit will deliver about 2.73 amp-hr before its voltage falls to 1.13 volts on a discharge through 83.3 ohms for 4 hr a day. These conditions correspond to radio use. The average voltage during this discharge is 1.3. Individual cells, except those in assembled batteries, are enclosed in tight-fitting cartons of news pulp chipboard or strawboard paper to insulate the zinc container of the cell from its surroundings or the surface supporting it.

Claussen[7] has described the industrial manufacture of the 6-in. dry cells, and Table 25 gives the range of commercial

TABLE 25. COMMERCIAL DRY CELLS

Designation	Diameter		Height		Minimum voltage
	Inches	Millimeters	Inches	Millimeters	
AAA	$\frac{1}{2}$	13	1	25	
AA	$\frac{1}{2}$	13	$1\frac{7}{8}$	48	
A	$\frac{5}{8}$	16	$1\frac{7}{8}$	48	1.47
B	$\frac{3}{4}$	19	$2\frac{1}{8}$	54	1.48
C	$\frac{15}{16}$	24	$1\frac{13}{16}$	46	1.49
CD	1	25	$3\frac{3}{8}$	86	
D	$1\frac{1}{4}$	32	$2\frac{1}{4}$	57	1.50
E	$1\frac{1}{4}$	32	$2\frac{7}{8}$	73	1.50
F	$1\frac{1}{4}$	32	$3\frac{7}{16}$	87	1.50
G	$1\frac{1}{4}$	32	4	102	1.50
#6	$2\frac{1}{2}$	63	6	152	1.50

sizes.[8] Electrical characteristics and testing are well standardized.[9] Gillingham has described the advances in the dry-battery

[6] DANIELS, F., *Trans. Am. Electrochem. Soc.*, **53**, 45 (1928).

[7] CLAUSSEN, R. A., *Trans. Electrochem. Soc.*, **64**, 341 (1933).

[8] GILLINGHAM, C. A., American Standards Association Committee C-18, *Trans. Electrochem. Soc.*, **71**, 13 (1937).

[9] Electrical Characteristics and Testing of Dry Cells, *Natl. Bur. Standards (U.S.)*, *Circ.* 79 (1923).

industry.[10]   The modern No. 6 general-purpose cell shows an initial short-circuit amperage of 43, a deterioration of only 7 per cent in 6 months, a life of better than 77 hr in the heavy intermittent-service test and 250 days in the light intermittent test.   The small CD hearing-aid batteries have a 50-hr life in the heavy earphone service test.   Lawson[11] has discussed service characteristics of dry cells, and Ceader and Mead[12] the characteristics of flashlight batteries.

Ramsey[13] described a 1,000-volt battery for Geiger counters for unmanned balloons which measure radiation in the stratosphere.   The battery potential could not fall more than 0.1 per cent per week.

Wilke[14] described a dry cell of the Leclanché type which exhibits improved performance characteristics at low temperatures.   The cell is designed to operate at −40°C (−40°F).   The improved characteristics are obtained by incorporating lithium chloride in the dissolved condition in the liquid electrolyte of the cell.   Cells have been developed and produced which at −40°C give capacities of 10 to 20 per cent of those obtained at 21°C (70°F) depending on the severity of the drain.   The ordinary Leclanché cell as manufactured by the battery industry exhibits inferior performance characteristics at −18°C (0°F) and is entirely unsatisfactory at −23°C (−10°F).

The difficulties in producing a low-temperature dry cell can be understood by considering the reasons for failure of the standard dry cell.   When such a cell is gradually cooled to a low temperature, its internal resistance gradually rises for a time and then at a critical temperature it rises abruptly.   This corresponds to the temperature at which the electrolyte completely solidifies.   This rise of internal resistance is sufficient to prevent the cell from operating.   Therefore, the first and major problem is to prevent this rapid increase in the internal resistance of the cell.

The current in a cell is carried both by the electrolyte and by the conductive material of the depolarizing mix, which prefer-

[10] GILLINGHAM, C. A., *Trans. Electrochem. Soc.*, **68**, 159 (1935).

[11] LAWSON, H. E., *Trans. Electrochem. Soc.*, **68**, 187 (1935).

[12] CEADER, J. D., and MEAD, T., *Trans. Electrochem. Soc.*, **68**, 207 (1935).

[13] RAMSEY, W. E., *J. Franklin Inst.*, **225**, 401–409 (1938).

[14] WILKE, MILTON E., *Trans. Electrochem. Soc.*, **90**, 433–440 (1946).

ably is Shawinigan black.[15]   The conduction through the black is electronic and is little affected by temperature.   The conduction through the electrolyte, being ionic, is dependent on the temperature.   The temperature affects both the viscosity of the electrolyte and the ionic mobility.

The electrolyte can be maintained in a liquid state by means of antifreeze agents such as alcohol or ethylene glycol, but the conductivity of such solutions at $-40°C$ is low.   Certain salts such as $ZnCl_2$ and $CaCl_2$ may be added to reduce solidification or congealing of the electrolyte at $-40°C$, but the viscosity and resistance remain high.   High percentages of $ZnCl_2$ also have the disadvantage of tending to hydrolyze the starch of the paste electrolyte partition and to produce excessive corrosion of the zinc.   On the other hand, solutions containing lithium chloride are very fluid, and the addition of the LiCl in the proper proportions to the electrolyte improves its conductivity at $-40°C$. These solutions show no detrimental effect on starch and do not affect shelf life adversely to an appreciable extent.

Magnesium–Silver Chloride Cell.[16]   At the beginning of the Second World War, a serious need arose for extremely lightweight, small-size, high-powered batteries.   This was necessitated by the many advances in electronic equipment for the armed forces.   The storage batteries and dry cells were either too large or did not have the desired capacity to meet the demands of the new lightweight and small-size electronic equipment. Early experience showed that an indefinite storage life was necessary for batteries to be used in all parts of the world.

The magnesium–silver chloride battery was developed as a reserve-type battery with the electrolyte to be added just prior to use.   A compact, simple, and efficient design of spirally wound cells was developed which is used in batteries with capacity over about 5 amp-min.   The positive electrode of each cell consists of silver foil, 0.001 to 0.003 in. (25 to 76 microns) thick, coated with electrolytically formed silver chloride on both sides, with wire leads welded on.   The electrochemical equivalents of the deposits range from 0.75 to 5.0 amp-min per sq in. (0.12 to 0.78

---

[15] An acetylene black.   WITHERSPOON, R. A., and CADENHEAD, A. F. G., *Trans. Electrochem. Soc.*, **70**, 52 (1936).

[16] MULLEN, J. B., and HOWARD, P. L., *Trans. Electrochem. Soc.*, **90**, 529–544 (1946).

amp-min per cm²) depending on current, life, and output required in the end use. The negative electrode consists of commercially pure magnesium foil of the same width, to which a similar wire lead is welded. The two electrodes are wound spirally together, with dry absorbent paper interleaved between the two electrodes. This forms a cylindrical cell with wire leads at the ends. The cell thus formed in its dry condition is inert and will keep indefinitely. The absorbent paper is an effective barrier between the silver chloride and magnesium electrodes. When saturated with an electrolyte, the absorbent paper becomes a conductive medium, and the cell can be discharged through a suitable resistance.

To make a battery of two or more cells, it is convenient to wrap the first cell with a layer of an insulator such as plastic film or varnished paper, after which the second cell is wound on like the first and concentric with it. This "concentric capsule" construction is applicable to low-voltage batteries for high and low rates of discharge where space and weight are at a premium.

For high-voltage applications, in which current and total output are low, the batteries are preferably made up in flat-cell form. Area of these cells ranges from 0.59 to 2.625 sq in. (3.78 to 16.8 cm²). In such cells the silver chloride is formed on only one side of the silver sheet. Batteries are made up by stacking plates with absorbent paper between the electrodes of each cell and insulation between adjacent cells.

The batteries are manufactured at a temperature of 27°C (80°F) at a relative humidity of 20 per cent, or an absolute humidity of 0.0045 lb of water per pound of dry air. Such air has a dew point of 3.33°C (38°F). The batteries are packaged in sealed cans in this atmosphere with a small quantity of silica gel as desiccant. Under these conditions, storage life is excellent.

At the time of use, the battery is removed from the sealed container and is activated by immersion in common or salt water to saturate the absorbent paper. It may be discharged either after removal from the water or while immersed continuously, *i.e.*, in the case of low-voltage batteries.[17] This eliminates the necessity of special electrolyte chambers, or storing a special electrolyte, since water is universally available.

[17] Specially designed cases for high-voltage batteries permit operation while continuously submerged.

When tap water is used as electrolyte, the low initial concentration of ions causes a comparatively slow rise in voltage for the first few seconds; but chloride and magnesium ions are rapidly produced by the cell action, which increases the conductivity of the electrolyte. Voltage ordinarily rises to nearly the peak within 1 to 2 min. If faster voltage rise is required, sea water or a dilute salt solution is used to supply sufficient ions at the start.

Figure 39 shows the comparative shapes of typical discharge

Fig. 39.   Typical discharge curves of three types of batteries. curve 1, perchloric acid type; curve 2, magnesium–silver chloride type; curve 3, dry cell.

curves of Leclanché, perchloric acid, and magnesium–silver chloride cells.

The principal advantages of the magnesium–silver chloride battery are that it is light in weight, small in size, and can be stored indefinitely in hermetically sealed containers without serious loss of capacity. Over-all averages of 12.9 amp-hr and 19.4 watt-hr per lb (28.4 amp-hr per kg and 43 watt-hr per kg) of battery on production units and 18.4 amp-hr and 22.6 watt-hr per lb (or 40.5 amp-hr per kg and 50 watt-hr per kg) of cell alone, are obtained.

The battery operates at high terminal voltage under high and low discharge rates. The data presented show that for low rates, from 10 milliamp to 10 amp, the voltage per cell is maintained between 1.42 and 1.50 volts. Change in ambient temperature has little effect on output. The discharge voltage remains flat over the major portion of the discharge.

Silver Oxide–Zinc–Alkali Cell.   Denison[18] described the characteristics and construction of experimental cells as shown in

[18] DENISON, I. A., *Trans. Electrochem. Soc.*, **90**, 387–403 (1946).

Fig. 40. The electrolyte was 25 per cent KOH with electrolytically formed Ag_2O_2 as one electrode and zinc as the other. The sensitivity of Ag_2O_2 to reduction by agents used as materials of construction in the cell was a severe disadvantage, but the discharge at a very high rate was an advantage.

The system has been the subject of numerous investigations and has been known for some time. A battery based on this system was patented in 1910 by Morrison,[19] and another patent
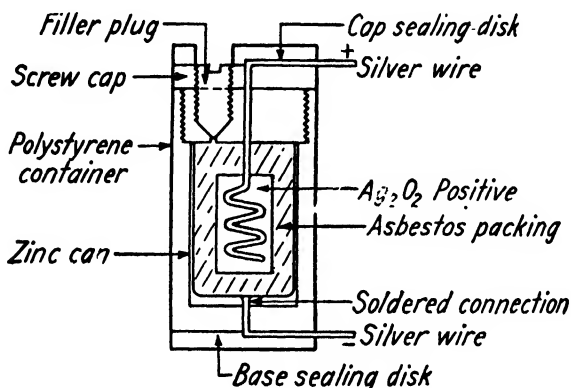
FIG. 40. Silver peroxide–zinc cell. Actual size.

for a similar battery was issued to Andre[20] in 1943. This system was also investigated by Zimmerman.[21] In some cases electrodes other than zinc were used as the negatives. Thus in 1902 Jungner[22] patented a battery having silver oxide positives and cadmium negatives. Later Jirsa[23] investigated the use of iron negatives.

The reaction of the system is

$$Ag_2O_2 + 2Zn + 2KOH = 2Ag + 2KHZnO_2$$

A cell based on the silver oxide–zinc–alkali system has the advantage of being adaptable under a variety of conditions. It

[19] MORRISON, W., U.S. Patent 976,092 (1910).

[20] ANDRE, H. G., U.S. Patent 2,317,711 (1943).

[21] ZIMMERMAN, J. H., *Trans. Electrochem. Soc.*, **68**, 231–249 (1935).

[22] JUNGNER, E. W., U.S. Patent 692,298 (1902).

[23] JIRSA, F., *Z. Elektrochem.*, **33**, 129–134 (1927).

is light in weight and will furnish current at a steady voltage even at high discharge rates. The limitations of the cell are that it is a primary source of current and, since its shelf life is poor, it must be filled with electrolyte just before being used. As a result, all the current to be drawn from the cell must be drawn at one time.

Perchloric Acid Cell. The cell contains plated lead dioxide positive plates, metallic lead negative plates, and aqueous perchloric acid electrolyte. The soluble nature of the discharge product, lead perchlorate, permits relatively high currents to be drawn from the cell at temperatures as low as $-20°C$. Discharge data at current densities from 0.045 to 3.33 amp per sq in. (0.70 to 51.6 amp per dm^2), temperatures from -40 to $+40°C$, and acid concentrations from 40 to 73 per cent are given by White and his associates.[24]

The perchloric acid cell was developed by Schrodt, Craig, and Vinal[25] for small lightweight batteries for use with radio sonde equipment. The over-all chemical reaction during discharge has been represented as follows:

$$PbO_2 + Pb + 4HClO_4 = 2Pb(ClO_4)_2 + 2H_2O$$
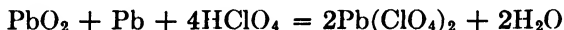
Acid efficiencies at each concentration based on the equation approach 100 per cent as the current density is reduced. Efficiencies greater than 100 per cent at low rates and high temperatures indicate a two-stage discharge process under these conditions with the formation of basic perchlorates as reaction products.

Positive plates are best prepared by plating a dense deposit of lead dioxide on an inert, conducting grid. Lead dioxide can be anodically plated from a lead nitrate bath.[26]

The powerful oxidizing conditions accompanying the plating of lead dioxide anodically also tend to dissolve most anode bases. Schrodt, Craig, and Vinal[27] employed palladium as a positive

[24] WHITE, J. C., POWER, W. H., McMURTRIE, R. L., and PIERCE, R. T., JR., *Trans. Electrochem. Soc.*, **91**, 73–94 (1947).

[25] SCHRODT, J. P., CRAIG, D. N., and VINAL, G. W., Report of the National Bureau of Standards to the Navy Department, Bureau of Ships, NBS Project 1911 (October, 1943).

[26] FERCHLAND, P., and NUSSBAUM, J., U.S. Patent 900,502 (1908); KATO, Y., British Patent 456,082 (1935).

[27] SCHRODT, CRAIG, and VINAL, *op. cit.*

grid material, since the plates were tiny and did not require large quantities of the precious metal. The cost of this material for larger and higher rate cells would be prohibitive, however, since large grid areas would be required. The application of nickel as a base for lead dioxide anodes[28] suggested its use for positive grids. To conserve this metal or to lighten the grid weight, nickel-plated aluminum, iron, or copper has been used.

Discharge characteristics of the perchloric acid cell depend on current density, acid concentration, and temperature. Commercial 71 per cent perchloric acid can be used as an electrolyte with good efficiency at temperatures of 25°C or higher and low current densities. As the current density is increased or the temperature lowered, the acid must be diluted for efficient operation of the cell.

The perchloric acid cell has limitations for general use. No positive grid material other than the precious metals has been found which will resist attack in contact with perchloric acid and lead dioxide for more than a few days. Cells using nickel grids must not be filled with acid until immediately before discharge. The dry battery in storage should last indefinitely.

R.M. or Ruben Cell. During the Second World War and for many years prior, there was a need for dry batteries to operate portable equipment requiring a high ratio of ampere-hour capacity to volume at higher current densities than were usually considered practical for the conventional dry cell. Ability to withstand storage under tropical conditions was also essential.

The development of a new cell to meet these conditions was undertaken at the request of the U.S. Army Signal Corps and resulted in the type of cell generally referred to as the R.M. Cell.[29] This cell comprises the electrochemical system $Zn|Zn(OH)_{2(solid)}$ KOH_{aq}^{-}. $HgO_{(solid)}|Hg$ and has a rated capacity of 200 milliamp-hr for each 1.6 g unit of active material. The open-circuit voltage of the cell is nominally 1.34 volts and the initial closed-circuit voltage under normal loads varies from 1.24 to 1.31 volts, depending on the load applied. The discharge curves obtained with the cell on normal drains are substantially flat, thus ensur-

[28] KATO, Y., and KOIZUMI, K., *J. Electrochem. Assoc. Japan*, **2**, 309 (1934); KATO, Y., SUGINO, K., KOIZUMI, K., and KITAHARA, S., *Electrotech. J.* (Japan), **5**, 45–48 (1941).

[29] RUBEN, SAMUEL, *Trans. Electrochem. Soc.*, **92**, 183 (1947).

ing reasonably uniform voltage output.[30]   The utilization of active materials is approximately 80 to 90 per cent and is efficient compared with other types of commercial dry cells.   The service obtained from the cell under high current drains is approximately four to seven times that of conventional dry cells of equivalent volume when discharged to the usual cutoff potentials of 0.75 to 1.0 volt.

Two basic designs are used, one making use of a "roll anode" and the other of a "pressed-powder anode" construction.   The roll-anode cell structure was the first design to go into large-scale production.   The pressed-powder anode cell, which incorporates such improvements as additional volume reductions for given

TABLE 26.   COMPARISON OF AVERAGE OUTPUT OF BATTERIES

Type of battery	Amp-hr/ lb (*)	Av. watt- hr/lb (*)	Av. amp- hr/cu in. (†)	Av. watt- hr/cu in. (†)
Lead acid battery:				
Range	4 9–6 5	9 6–11 5	0 44–0 51	0.92–0 99
Average	5 6	10 5	0 47	0 96
Nickel (Edison):				
Range	8 6–10 4	10 4–12 6	0 89–0 96	1 07–1 15
Average	9 6	11 7	0 92	1.11
Dry-cell battery:(‡)				
Range	1 5–1 65	1 87–2 07		
Average	1 55	2 0	0 12	0 15
Perchloric acid battery:				
Range	6 5–8 6	8.8–17 1		
Average	7 5	12.9	0.895	1.7
Magnesium-silver chloride, water-acti- vated:				
Average.	12.9	19.4	0.548	0 854
R. M. battery:				
Average	11 6	13 1	1 37	1 53

(*) There are 0.4536 kg per lb.

(†) There are 16.4 cm³ per cu in.

(‡) Figure of 150 milliamp drain taken since comparison is nearer to lower drains on other types of batteries.

NOTE: Figure for the secondary batteries and dry cell were obtained from Dr. G. W. Vinal's text on storage batteries and Bureau of Standards CL-677.

[30] FRIEDMAN, MAURICE, and MCCAULEY, CHARLES E., *Trans. Electro-chem. Soc.*, **92**, 195 (1947).

watt-hour capacities, may supplant the roll-anode cell for commercial applications.

Mullen and Howard[31] compared the average output of a number of battery systems as given in Table 26. The magnesium–silver chloride water-activated battery showed the highest watt-hour output per pound of battery. Figure 41 shows com-
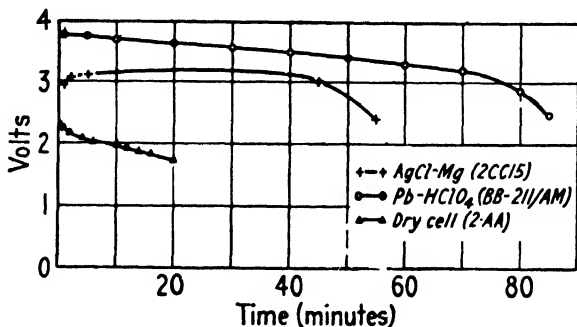
FIG. 41. Comparison of magnesium–silver chloride perchloric acid, and dry-cell batteries. Magnesium–silver chloride battery, two-cell type 2CC15. Positive plate area 24.5 sq. in.; activated in tap water for 60 sec. Perchloric acid battery type *BB*-211/*AM*. Dry cell, two-*A A* cells in series. Load 10 ohms continuous.

parative discharge curves for the dry cell, the perchloric acid, and the magnesium–silver chloride cells.

[31] MULLEN, J. B., and HOWARD, P. L., *Trans. Electrochem. Soc.*, **90**, 529–544 (1946).

CHAPTER 11

SECONDARY CELLS

Cells which are reversible to a high degree, in that the chemical conditions may be restored by causing current to flow into the cell on charge, are classed broadly as storage batteries or electric accumulators. The Daniell or gravity cell as well as the Lalande is reversible to a high degree, but these cells have practical disadvantages preventing their use as storage batteries. The form in widest commercial use is the Pb-H_2SO_4 type. The only other form of any prominence in the United States is the Ni-Fe-caustic cell, often termed the "Edison cell."

In 1859 as a result of his experiments on electrolytic polarization, Planté devised a cell for the storage of electrical energy consisting of two sheets of lead separated by strips of rubber, rolled into a spiral form, and immersed in a dilute (about 10 per cent) solution of H_2SO_4. He found it possible to increase the capacity of the cell materially by a process now known as "formation." Following periods of charge, he discharged the cell or allowed it to rest, during which time local action transformed the covering of peroxide on the positive plate into $PbSO_4$. From time to time he reversed the polarity and repeated the process of charge and discharge to build up the capacity of the cell.

The positive pole of a cell is that one from which the current flows into the external circuit. In storage-cell practice a positive plate is one which is connected to the positive pole, and the negative plate is one which is connected to the negative pole.

For extended commercial use a storage cell should have high capacity per unit of weight. Chemical effects, even though slight, that cause deterioration or loss of stored energy should be absent. The transformation of electrical into chemical energy as in charging, and of chemical into electrical energy in discharging, should proceed nearly reversibly. An ideal storage cell should have low resistance, have simplicity and strength of construction, be durable, and be producible at low cost. In the

past a large number of storage-cell constructions and systems were proposed. Almost all of them had disadvantages which prevented their commercial adoption, so that at the present time only two secondary cells need to be considered. The Pb-H_2SO_4 type is in universal use. It does not suffer from deteriorating chemical effects, shows almost reversible transformation of electrical into chemical energy and vice versa, has low resistance, can be used for long periods with proper care, and has low first cost. It does not have as high capacity per unit of weight as might be desired; and while its construction is simple, the mechanical strength of the lead plates is low. On the other hand, the Ni-Fe-caustic potash cell, also known as the Edison, shows high capacity per unit of weight, absence of deteriorating chemical side reactions, and ability to withstand long, continued use. Its first cost, due to expensive materials and complex construction, is high, but the cell is mechanically strong and durable. It has the disadvantage, however, that it shows charging and discharging losses due to the incomplete reversibility of the electrical and chemical energy transformations in the cell system.

LEAD SECONDARY CELLS

The Pb-H_2SO_4 cell system is $PbO_2|H_2SO_4|$sponge Pb. On discharge of the cell, both the peroxide on the positive plate and the lead on the negative plate are quantitatively converted into $PbSO_4$ according to the reactions

$$PbO_2 + H_2SO_4 = PbSO_4 + H_2O + O$$

and

$$Pb + H_2SO_4 = PbSO_4 + 2H$$
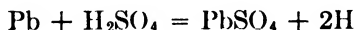
which may be combined into the reaction

$$PbO_2 + Pb + 2H_2SO_4 = 2PbSO_4 + 2H_2O$$

which, when read from left to right, is the equation of discharge and, inversely, the reactions during charge.

The reaction given above is that of the double-sulfate theory, the significance of the term being due to the fact that $PbSO_4$ is formed on both positive and negative plates during the process of discharge. A large number of other theories have been

proposed[1] but have not found acceptance. The double-sulfate theory is capable of thermodynamic proof. Although the theory gives us an equation for calculating the performance of the cell, it does not tell us about the actual processes taking place at the positive and negative plates. Vinal[2] gives pictures (Fig. 42)

Discharge Reactions
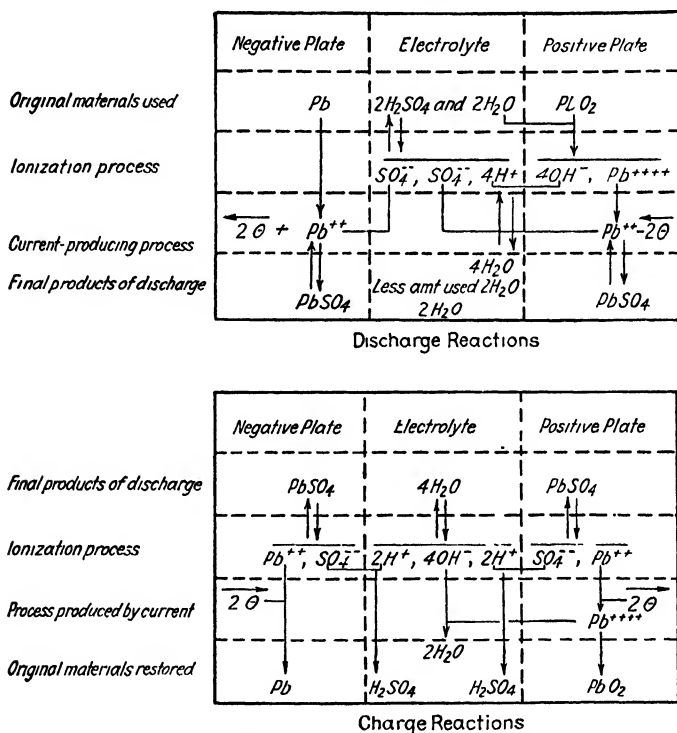
Charge Reactions

Fig. 42. Discharge and charge reactions of lead cell.

of discharge and charge reactions taking place in the cell, which are taken from his book by permission.

Cell Construction. Lead storage batteries are made in a wide range of sizes and capacities from very small elements for experimental work with two or three cells, up to units of very high capacity weighing several tons for central station work. For

---

[1] For discussion of the many theories proposed by investigators, see G. W. Vinal, "Storage Batteries," 2d ed., p. 152, John Wiley & Sons, Inc., New York, 1930.

[2] *Ibid.*, pp. 157, 159.

stationary cells, containing vessels for the smaller and medium units are of glass; for the larger ones, lead-lined wood. Containers for batteries up to several thousand ampere-hours capacity are of glass. Containers for portable batteries are almost universally made of hard rubber or rubber mixtures. The plates in the cells are hung vertically, positives and negatives alternately, plates of the same kind being connected in parallel to external studs or connecting posts. The plates may be guided by grooves in the side of the cell and held apart and prevented from short-circuiting by separators, usually sheets of wood specially treated and machined. In some cases the wood is replaced by perforated sheets of rubber. In general, the plates are suspended in the cell so that there is a free space at the bottom which can serve as a reservoir of acid and allow a place where conducting material dropping from the plates can fall without short-circuiting the plates. Usually the two end plates in a cell are negatives. Positive plates if active only on one side, become deformed as the volume of their active masses changes during working.

The concentration of H_2SO_4 in the electrolyte varies for different types of cells, corresponding to the specific gravities, showing a range for fully charged cells of 1.200 to 1.300. The most common types employed in connection with automobiles for starting and lighting show specific gravities of 1.270 to 1.300. The chemical reactions within the cell practically limit the higher concentrations of acid to 1.300 specific gravity.

Types of Plates. The active materials, the PbO_2 on the positive plate and the sponge lead on the negative, are crystalline in structure and the intergrowth of the crystals holds the masses together. It is probable that the positive active material is a hydrated peroxide of lead as it exists in the cell. Many commercial modifications of plates have been proposed and are in use either for forming the active materials in place or for applying them and holding them in place by some mechanical structure. In general the plates may be of the Planté type comprising a mass of lead, usually of flat form, with a highly developed surface on which the active material is electrochemically formed as a coherent layer; or pasted plates in which the active materials are cemented masses supported in a grid, usually of lattice form.

Planté Plates. Planté plates are prepared from lead blanks which have been cast, rolled, cut, and stamped. A number of

different methods have been used for increasing the surface of these plates. In one the plate is "plowed" so that fine furrows are made and leaves of lead thrown up on the plate. In others the blanks are swaged by blocks having designs cut in their surfaces so that recesses are produced in the finished plate. In another case the plates are spun to increase the surface. In Europe highly developed surfaces have been obtained by casting. In the so-called "Manchester plate" (Fig. 43), heavy grids of
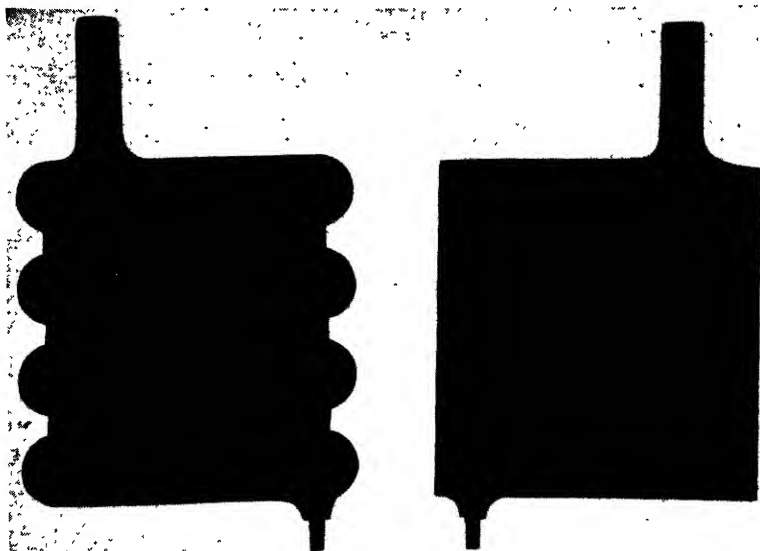
Fig. 43. A Manchester-positive and a box-negative plate. (*The Electric Storage Battery Company.*)

antimonial lead are cast with a large number of round holes into which buttons of soft lead with corrugated surfaces are pressed, the buttons being prepared from lead ribbon. The holes are made with a slight bevel so that, as the lead button grows during the operation of the cell, it becomes more and more tightly locked in the supporting grid.

The active materials of the Planté plate are obtained by oxidizing the surface of the lead plate or reducing this material to sponge lead. In the original process used by Planté, the plates were alternately charged and discharged with occasional reversals of the charging current until the plates had acquired sufficient capacity. The method requires considerable time and a large

amount of electrical energy. The common method at the present time involves the use of "forming" agents which attack the lead of the plate. These are usually salts of some acid, such as HNO_3, or a large number of other materials such as chlorates, perchlorates, chlorides, fluorides, oxidizing agents such as bichromates and permanganates, and reducing agents such as formic acid, oxalic acid, alcohol, hydroxylamine, and sulfurous acid. The forming process in which these addition agents are used is practically confined to the positive plates which are the anodes in the forming bath. Negatives are obtained by a reversal of the positive plates during which the PbO_2 on their surfaces is reduced to sponge lead.

Pasted Plates. Pasted plates (Fig. 44) consist of grids or
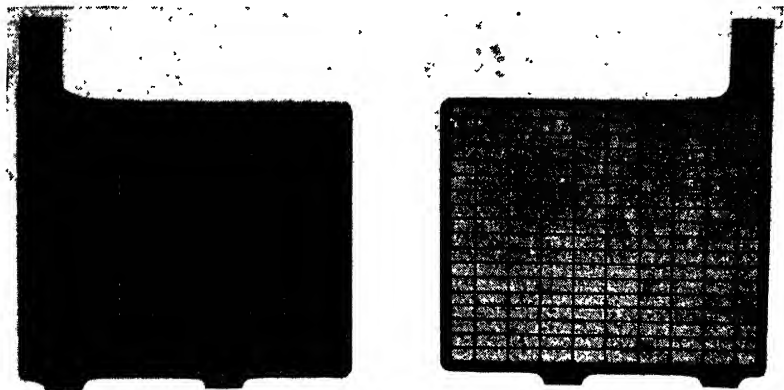
Fɪɢ. 44. Pasted positive and negative plates. (*The Electric Storage Battery Company.*)

cast antimonial lead forms in the openings of which a paste, generally made by mixing litharge (PbO) or red lead (Pb_3O_4) or a combination of these with a dilute solution of H_2SO_4, is placed. Many variations in the conditions of preparing and applying the paste are possible and differ with different manufacturers. It is probable that these two reactions occur:

$$Pb_3O_4 + 2H_2SO_4 = 2PbSO_4 + PbO_2 + 2H_2O$$
$$PbO + H_2SO_4 = PbSO_4 + H_2O$$
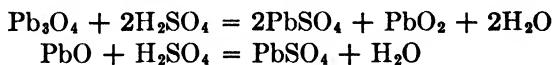
In addition, it is probable that hydration of the lead oxide also occurs. Sometimes pulverized lead is used in connection with the manufacture of plates, and expanders consisting of

relatively inert materials are added in amounts of a fraction of a per cent to the materials for negative plates. Lampblack, $BaSO_4$, graphite, and various forms of carbon have been used. Their function is to prevent the contraction and solidification of the sponge lead of the finished negative plate.

The pasted grids are allowed to dry and harden and are then electrolytically oxidized and reduced in either dilute H_2SO_4 or a sulfate solution. This formation process is carried out either in lead tanks or in glass or rubber vessels holding a large number of plates. The positives and negatives are usually formed together, although the latter require somewhat more time than the former. Formation is seldom complete in a day but usually occupies several days. After this time the plates are washed and assembled in cells.

Cell Characteristics. Pasted plates have the disadvantage that they are mechanically weaker than Planté plates, and the active material tends to fall out in time, particularly at high current density. One manufacturer employs positive plates with a paste of high capacity, adapted for use with a spun-glass retainer of a porous nature and low resistance. The glass layer prevents the active material from falling out of the plates. Another maker has developed a pasted plate which is very hard, of high capacity, and porous. A slotted, thin, tough, hard-rubber retainer is used on both sides of the positive plate. This retainer, in addition to the wedging of their elements in the rigid container, furnishes the mechanical support necessary for long life. Pasted plates show a higher capacity per unit of weight, however, than do Planté plates. The capacity of a storage cell is stated in ampere-hours at some normal rate of discharge, the 8-hr rate being standard with lead cells of the stationary type. The capacity of a cell with a definite type and thickness of plate is in proportion to the plate area. The emf or open-circuit voltage of any storage cell depends wholly upon its chemical constituents and not in any way upon the number or total area of the plates. It varies further with the strength of the electrolyte, with the temperature, and to a minor extent with the state of charge of the plates, internal resistance of the cell, polarization, and acid concentration effects. Per ampere-hour of discharge, the amount of active material converted into $PbSO_4$ is 0.135 oz of sponge lead and 0.156 oz of PbO_2, independent of the rate of discharge. The

amount of active material actually present in the plate is some three to six times that which under normal discharge of the cell is converted into $PbSO_4$. Part of this excess is present to give long life to the plates.

The open-circuit voltage of a lead cell varies from 2.06 to 2.14,
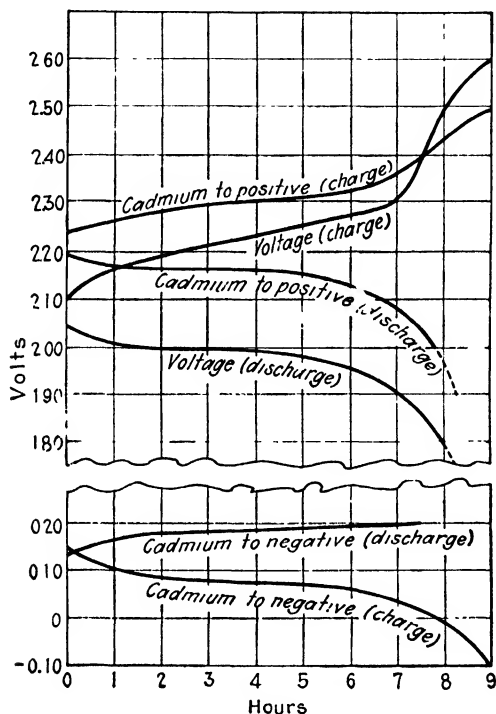
FIG. 45. Typical charge–discharge curves of lead storage battery.

according to the strength of the electrolyte and the temperature, and may be calculated from the formula

$$E = 1.850 + 0.917(G - g)$$

where G is the specific gravity of the electrolyte and g the specific gravity of water at the cell temperature.

Typical charge and discharge curves for the stationary type of lead cell are given in Fig. 45. It is often desirable to determine the relative performance of positive and negative plates in a cell. This may be done by taking the voltage between either group

and a reference electrode such as zinc, sponge lead, or preferably cadmium. Cadmium curves are included in the diagram.

Vinal, Craig, and Snyder[3] studied the addition of small amounts of cobalt, nickel, and iron sulfates to the electrolyte of commercial batteries which were then subjected to 150 cycles of charge and discharge. Cobalt decreased the charging potential of positive plates, and nickel decreased the charging potential of negative plates. Iron showed no significant effect on the potentials of either plate. Cobalt reduced the corrosion of some of the positive plates but had a harmful effect on the wood separators. Decreased positive plate potentials are of interest because they may permit the use of lead alloys free from antimony.

Lead storage batteries are used for stand-by electric-power services where the pasted-plate type is preferred; for electric vehicles; train lighting; gasoline engine and automobile starting, lighting, and ignition; signaling and control work; as well as many other applications.

ALKALINE SECONDARY CELLS

There are only two alkaline storage cells in commercial use in the United States. The first is the Hubbell consisting of the system Ni threads and Ni oxide|KOH|Fe, used in miners' lamps. The second is the more important Edison battery consisting of the system finely divided $Ni + Ni$ peroxide|21 per cent KOH|finely divided Fe. The active materials of the Edison cell consist of nickel peroxide for the positive plate and finely divided iron for the negative. Typical cell construction is shown in Fig. 46. Small amounts of LiOH are added to the electrolyte, and certain amounts of mercury are incorporated with the iron of the negative plate to overcome the passivity of the iron, while layers of flake nickel are added to the positive plate nickel oxide to increase its conductivity. The reactions of the cell are

$$8KOH + 6NiO_2 + 3Fe = Fe_3O_4 + 2Ni_3O_4 + 8KOH$$

or

$$6NiO_2 + 3Fe = Fe_3O_4 + 2Ni_3O_4$$
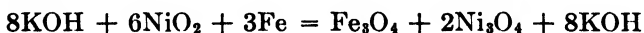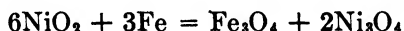
which, when read from left to right, are the reactions of discharge

[3] VINAL, G. W., CRAIG, D. N., and SNYDER, C. L., *J. Research Natl. Bur. Standards*, **25**, 417–420 (1940). (*Research Paper* 1335.)

NEGATIVE POLE
HARD RUBBER
GLAND CAP

CELL COVER

STUFFING BOX
GASKET

NEGATIVE GRID

NEGATIVE POCKET
[IRON OXIDE]

PIN INSULATOR

SIDE INSULATOR

SOLID STEEL
CONTAINER

SIDE ROD INSULATOR

VALVE   FILLER CAP   POSITIVE POLE

COPPER WIRE SWEDGED
INTO STEEL LUG
CELL COVER WELDED
TO CONTAINER
STUFFING BOX
WELD TO COVER
GLAND RING
POLE INSULATOR
SPACING WASHER
CONNECTING ROD
POSITIVE GRID
GRID SEPARATOR
SEAMLESS STEEL
RINGS
POSITIVE TUBE
[NICKEL HYDRATE AND
NICKEL IN LAYERS]

CORRUGATIONS

SUSPENSION BOSS

CELL BOTTOM
WELDED TO SIDES

FIG. 46. General construction of the Edison cell. (*Edison Storage Battery Company*.)

and, inversely, those of charge. It is probable that the iron and nickel oxides are both hydrated. In charging the cell, the electrolyte density does not change as in the lead storage cell, but concentration changes of the electrolyte in the pores of the active materials do take place with perhaps the formation of higher oxides of nickel.

Positive Plates. The positive plates are filled with nickelous hydroxide, which is converted to a higher oxide of nickel by the formation process. Additions of flake nickel are made to increase the conductivity of the mass, as the nickelous hydroxide is a nonconductor. Alkaline cells, other than those of Edison, use graphite for this purpose. The positive plate consists of a

nickel-plated steel frame into which are pressed perforated tubes filled with alternate layers of nickel hydrate and metallic nickel in very thin flakes.   The tube is made from a thin sheet of steel, nickel-plated and perforated, and has a spirally lapped joint. The negative plate consists of a grid of nickel steel with oblong openings into which perforated steel boxes containing finely divided iron with mercury are placed.

The flake nickel used in the Edison cell consists of small squares, $\frac{1}{16}$ in. on a side and about 0.00004 in. thick.   It is made by a nickel-plating process in which revolving copper cylinders are carried by a crane and dipped alternately into copper- and nickel-plating baths for a time sufficient to deposit thin layers of the metal.   The alternate plating of copper and nickel is repeated 125 times, a process taking about 5 hr, after which the copper-nickel sheet is stripped from the cylinders and cut into $\frac{1}{16}$-in. squares.   The copper is then dissolved chemically, leaving the nickel as thin flakes which in a final washed, centrifuged, and dried state weighs only 3.6 lb per cu ft.

The tubes used to hold the active material on the positive plates are made from cold-rolled carbon-steel ribbon, which is perforated, nickel-plated, and annealed in a hydrogen atmosphere. The ribbon is wound spirally to form the tubes, the seams being lapped and swaged flat.   The finished tubes are either $\frac{1}{4}$ or $\frac{3}{16}$ in. in diameter and $4\frac{1}{2}$ in. long.   They are filled with alternate layers of nickelous hydroxide and flake nickel so that there are about 630 layers in a tube, the tube having 14 per cent of its contents as flake nickel.   After the tubes are filled, the ends are pinched together to form terminals by which the tubes are clamped into the steel grid or frame.   Each tube is reinforced by eight seamless nickel-plated steel rings, used to prevent possible bursting of the tube because of the swelling of the active material which takes place during forming.

Negative Plates.   Negative plates consist of a grid with a number of pockets in which perforated nickel-plated steel boxes are placed, the boxes containing black oxide of iron (FeO) mixed with about 6 per cent of mercury oxide.   When the plate is first charged, this is reduced to mercury and the FeO to metal. The necessary number of positives for any particular size of cell are mounted on a steel rod which passes through the holes at the tops of the plates.   Plates are separated from one another

by means of washers fitting on this rod and are locked in place by a lock washer and nut on the end of the rod. Negatives are assembled in a similar manner, and the group of positive and negative plates are intermeshed to form the cell element, the plates being separated by hard-rubber pins. Side separators made of flat sheets of hard rubber are used around the outside of the element to insulate it from the nickel-plated sheet-steel can employed as a cell container.

Cell Characteristics. Characteristic normal charge and discharge curves for the Edison battery are given in Fig. 47. The
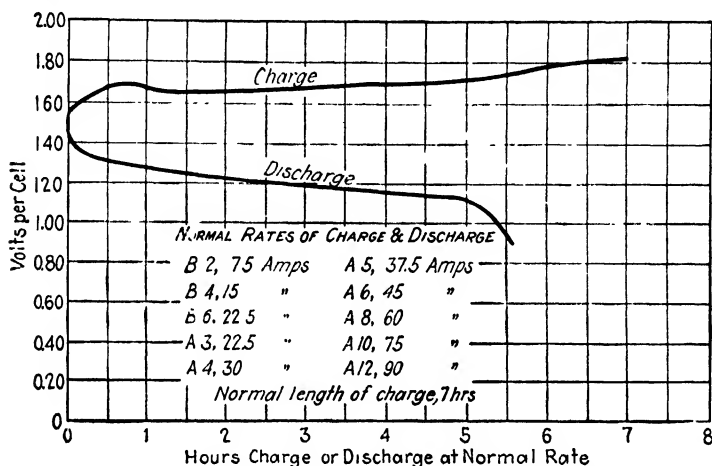
Fig. 47. Normal charge and discharge curves for Edison alkaline cells.

average voltage on discharge is approximately 1.2, the initial open-circuit voltage 1.5, and the final voltage at the end of discharge a little less than 1.

Edison cells are used for ignition and lighting of gasoline motor cars, but because of their high internal resistance are not used for motor starting. They find wide application in electric vehicles, storage-battery streetcars, mining locomotives, and industrial trucks. In contradistinction to lead storage batteries, they are not used for load regulation in power systems because of their heavy voltage drop at high discharge rates. The commercial cells show ampere-hour efficiencies of 82 per cent and watt-hour efficiencies of 60 per cent, with an average capacity of about 13 watt-hr per lb of cell.

Féry[4] has suggested a "dry accumulator" Sn|dilute H_2SO_4|PbO_2, filled with ceramic material and sealed, which gives a voltage of 1.75. Haring and Compton[5] studied the generation of SbH_3 by lead cells. Haring and Thomas[6] and Schumacher and Phipps[7] investigated the electrochemical behavior of lead, lead-antimony, and lead-calcium materials. They recommended the lead-calcium alloy containing 0.04 to 0.10 per cent Ca for storage-battery grids, in place of the widely used lead-antimony alloy, and for Planté plates, instead of lead. The lead-calcium cells retain their charges for longer periods than lead-antimony cells and are more efficient. The lead-calcium alloy shows higher conductivity than the lead-antimony alloys.

According to the National Battery Manufacturers' Association, an average storage battery contains better than 23 lb lead per unit and in service shows a life greater than 2 years. Harned and Hamer[8] reported a summary of the molal electrode potentials and the reversible emfs of the lead accumulator from 0 to 60°C. Storage-battery life tests were discussed by Hatfield and Harner.[9]

Nickel-Cadmium Cell. A secondary battery developed by Accumulatoren Fabrik A.-G.,[10] Hanover, Germany, has positive plates of nickel powder sintered at 900 to 960°C for 1.5 hr in a reducing atmosphere onto a framed steel-mesh grid, impregnated with aqueous nickel nitrate of specific gravity 1.62, electrolyzed in aqueous NaOH of specific gravity 1.23 to deposit nickel hydroxide while a current of 8 to 10 amp per dm^2 (74.3 to 92.9 amp per sq ft) is passed for 10 to 12 min to generate hydrogen to keep the pores open, washed free of nitrate, and dried. The complete impregnation process is repeated four or five times to

[4] FÉRY, C. J. V., *French Patent* 748,630.

[5] HARING, H. E., and COMPTON, K. G., *Trans. Electrochem. Soc.*, **68**, 283 (1935).

[6] HARING, H. E., and THOMAS, U. B., *Trans. Electrochem. Soc.*, **68**, 293 (1935).

[7] SCHUMACHER, E. E., and PHIPPS, G. S., *Trans. Electrochem. Soc.*, **68**, 309 (1935).

[8] HARNED, H. S., and HAMER, W. J., *J. Am. Chem. Soc.*, **57**, 33–35 (1935).

[9] HATFIELD, J. E., and HARNER, H. R., *Trans. Electrochem. Soc.*, **71**, 583, 597 (1937).

[10] CHU, G. D., *Natl. Research Council Can., Elec. Eng. Radio Branch Rept.* ERB-172 (1947).

deposit a thick coat of active hydroxide.   Negative plates are made similarly by starting with 70 per cent copper-30 per cent nickel powder sintered at 880 to 920°C, impregnated with aqueous $CdCl_2$ of specific gravity 1.62, and electrolyzed at 10 to 12 amp per dm^2 (92.9 to 111.48 amp per sq ft) for 20 to 25 min to deposit $Cd(OH)_2$.   Six 60 by 70 by 2 mm (2.3 by 2.7 by 0.08 in.) positive plates and five negative plates separated by 0.8 mm (0.03 in.) diameter spacers of polyvinyl chloride are assembled into a polystyrene case having nonspillable caps sealed by Hg on sintered glass.   The internal resistance of a single cell is 2.5 $\times$ 10^{-3} ohm.

Nineteen such cells are assembled into a 10-amp-hr, 24-volt battery, KOH electrolyte d_{20} 1.245 is added, and the plates are formed by alternately charging and discharging at 2 amp as follows: 10 hr charge, 3 hr discharge; 7.5 hr charge, 5 hr discharge; 7.5 hr charge, discharge to 1.1 volts per cell.   Deterioration of the negative plate causes loss of capacity on standing fully charged or after 200 cycles, but the capacity can be recovered by slow discharge followed by rapid charge.   Tests show that discharge at 50 amp for 5 min reduces the voltage to 1.0 volt per cell; that the percentage reduction of capacity is the same as for the Pb-acid battery when the temperature drops to -7°C but is less at lower temperatures; and that the loss of capacity with rapid discharge is less than for the Pb-acid battery.   The capacity at -20°C is about 10 per cent larger than that of the Pb-acid cell.   The cell may operate below -40°C, but a high-density electrolyte, which shortens battery life, is required.

CHAPTER 12

RECTIFIERS AND LIGHTNING ARRESTERS

The phenomena of film formation on metal electrodes and the unusual polarizing effect of aluminum have long been known.[1] Aluminum, tantalum, bismuth, and antimony show similar effects in certain electrolytes at definite voltages and current densities. The same type of film formations occurs with almost any metal under suitable conditions.[2]

Film formation commonly causes a relatively small rise in anode potential, as a result of which metal solution continues with the production of ions of higher valency or is more or less replaced by anion discharge. In the case of metals like aluminum, nonporous films of high resistance are produced with resulting potentials of very large values. For example, aluminum in electrolytes, such as very dilute ammonium borates, carbonates, phosphates, and corresponding salts of the alkali metals, may form films which have breakdown resistances equivalent to 600 volts. The films formed have unusual electrical properties, in that they are characterized by the influence of impressed potential on their electrical resistance. A typical curve[3] for an aluminum anode film in an ammonium borate electrolyte is given in Fig. 48. The films are capable of conducting current more freely in one direction than another, a property employed in the electrolytic rectifier; their resistance decreases as the applied voltage is increased until they break down as insulators at critical voltages, a property on which the electrolytic lightning arrester depends; and the films in small thickness are capable of retaining substantial charges of electricity at potentials below the critical or breakdown value, as well as showing high dielectric strength, a property made use of in the electrolytic condenser. In another form the films are produced

[1] WHEATSTONE, C., *Phil. Mag.*, 10, 143 (1855).
[2] GÜNTHER SCHULZE, *Trans. Faraday Soc.*, 9, 266 (1913).
[3] SIEGMUND, H. O., *Trans. Am. Electrochem. Soc.*, 53, 203 (1928).
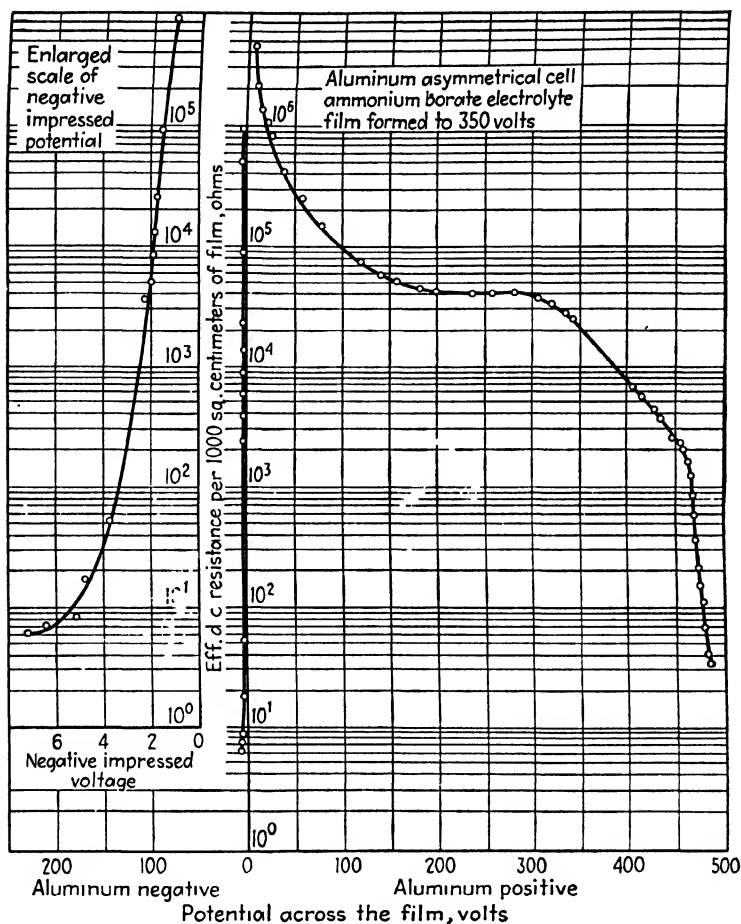
Fig. 48. Influence of impressed potential upon the electrical resistance of the film on the aluminum electrode. (*Siegmund.*)

for protection against corrosion, a process known as "anodizing" and discussed under electroplating.

During electrolysis the anode is visibly changed. Its resistance grows greater, and increases in voltage are necessary to maintain current flow. The film thickness increases until finally a potential is reached at which there is a scintillating spark discharge between electrolyte and electrode. At potentials near the breakdown voltage, the surface of the anode glows with a pale light,

readily visible in the dark.   Edwards[4] states that an aluminum-manganese alloy anode in a 0.1 per cent NaOH solution at 220 volts glows with a bright orange light which looks like hot metal. Anions give up their charges, the electrons passing through the dielectric layer of the film.

When filmed electrodes are employed as cathodes, the insulating layer may be readily destroyed with metals whose oxides are readily reducible, inasmuch as the films allow the discharge of H^+ ions.   Such cathodic reductions are industrially important in electrolytic cleaning, discussed under electroplating.   With metals like aluminum and tantalum, the persistence of the film makes the electrode of use as an electrolytic valve.   A lead anode and aluminum cathode in an electrolyte will allow current to pass; a potential reversal would result in an aluminum-filmed anode and lead cathode, whose resistance would be so high that only a very small "leakage current" could pass.   Such an arrangement is of use between a generator and a bank of cells being charged. If the generator should stop, the cells could not supply reverse current to the generator.
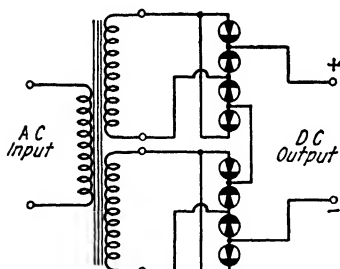
FIG. 49.   An electrolytic rectifier.

Electrolytic Rectifiers.   Electrolytic valves may be employed as rectifiers for the conversion of alternating to direct current. Arrangements such as those shown in Fig. 49 are employed. Four rectifier cells are connected as shown.[5]   The film formation on aluminum allows the passage of appreciable current only when the electrode is used as cathode.   From the figure it can be verified that the current produced on the right-hand circuit will be direct current and that both positive and negative waves of the alternating current are utilized.   The energy efficiency of the setup averages about 60 per cent.

Two types of electrolytic rectifiers have found industrial use. The first of these is the aluminum; the second, the tantalum rectifier.   A typical aluminum rectifier is shown in Fig. 50.   The

---

[4] EDWARDS, J. D., "The Aluminum Industry," Vol. II, p. 725, McGraw-Hill Book Company, Inc., New York, 1930.

[5] HOLLAND, W. E., *Trans. Am. Electrochem. Soc.*, **53,** 195 (1928).

anode is a 14 per cent Si iron alloy, the cathode a rod or block of aluminum containing copper of the order of 0.05 to 0.1 per cent copper. The electrolyte is dibasic ammonium phosphate solution to which potassium salts have been added to increase the conductivity of the electrolyte, and quantities of either malic or citric acid to give the resultant electrolyte greater capacity for holding aluminum in solution and extending the life of the rectifier. The copper impurity in the aluminum electrode plays an important role. When a rectifier is observed in the dark during operation at voltages approaching the sparking point, the pure aluminum will appear to be emitting a shower of reddish sparks, while the copper-aluminum will merely glow with the characteristic greenish light of a glowworm.

Fig. 50. Aluminum rectifier (*Philadelphia Storage Battery Company.*)

Holler and Schrodt[6] studied the wave form of the current passed by an aluminum rectifier. The anode film, with its high dielectric value and resistance, acts as a condenser and allows a small alternating current to pass, thus decreasing the rectification efficiency.

Many rectifier electrolytes have been proposed but only sodium, potassium, and ammonium phosphates, citrates, borates, and malates and their acids are commercially used. A good electrolyte should be highly conductive, be noncorrosive on the film-free electrode, be film-forming on the filmed electrode, and be noncorrosive to the base metal.

The tantalum rectifier consists of a lead anode, tantalum cathode, and an electrolyte of H_2SO_4 (sp gr 1.200), to which $FeSO_4$ is added as a depolarizing salt and small amounts of $CoSO_4$ to lessen the attack on the lead electrode. A rectifying action is due to the formation of a film of Ta_2O_5 which is porous and

[6] HOLLER, H. D., and SCHRODT, J. P., *Natl. Bur. Standards (U.S.), Technol. Paper* 265.

spongy. Oxygen gas is trapped in this film to form a gaseous layer entirely surrounding the tantalum electrode, with resultant valve or rectification action. The $FeSO_4$ depolarizing salt lowers the counter emf of the cell and thus increases its efficiency and capacity, as well as stabilizes the unit. Some slight corrosion of the lead electrode occurs, due to secondary chemical reactions. In most commercial rectifiers, the electrolyte is protected from evaporation by a layer of oil.

Lightning Arresters. The so-called "valve" type of lightning arrester, an example of which is the oxide-film arrester, operates on two basic principles, one determining the protection offered by the arrester and the other the ability of the device to prevent the flow of follow current after the impulse has passed. Effective protection is governed chiefly by the ability of the arrester to decrease its resistance with increase of current, so that the potential across the arrester will vary but little whether the flow of current be large or small. As the impulse current decreases following the discharge of lightning, the valve type of arrester is capable of so increasing its resistance that little or no system current follows.

The oxide-film arrester is made in either the pellet or the plate form. The former is manufactured for a.c. circuits of voltages up to 73,000. It consists of a number of litharge coated PbO_2 pellets with a gap in series between line and ground. The pellets, about $\frac{3}{32}$ in. in diameter, are placed in a porcelain tube and assembled in good electrical contact with metal electrodes at each end of the column, the column being proportional in length to the line voltage. One or more series gaps between the line and the pellet column isolate the pellets from continuous application of the line voltage but permit discharge at a definite voltage above normal.

The plate form of oxide-film arrester is designed for use on all a.c. circuits from 300 to 220,000 volts. It is made of a number of cells with a gap in series between line and ground. The cells are held together under moderate pressure and are arranged in sections or stacks according to the voltage and kind of circuit. Cells are disk-shaped, about $7\frac{1}{2}$ in. in diameter and $\frac{5}{8}$ in. thick, with an active area of approximately 23 sq in. Each cell is made of two circular brass plates crimped firmly to the edges of an annular piece of porcelain. The spaces between the plates

are filled with PbO_2, a powder of very low resistance. The inside of the plates is covered with a porous varnish film whose thickness is carefully controlled so that the film breakdown under lightning disturbances can be quite accurately predetermined. When a lightning voltage sparks over the gaps, it punctures the film on the metal plates of the cells. As soon as the film gives way, a discharge current flows through the cells to ground, thus relieving the lightning pressure.

A third important lightning arrester is the aluminum arrester for d.c. circuits, made up of groups of aluminum cells in series. The cell consists of two aluminum plates on which a film of $Al(OH)_3$ has been formed by chemical and electrochemical processes, the plates being immersed in a suitable electrolyte. The aluminum plates are held in glass jars filled with electrolyte and are supported rigidly from porcelain covers in such a way as to prevent them from vibrating and short-circuiting. When the arrester is connected to the circuit, a small leakage current flows through it and keeps the film on the plates, these films preventing a current flow through the arrester at normal voltages. If the voltage be suddenly increased, as from a lightning disturbance, a discharge current will flow through the arrester to ground, limited only by the internal resistance of the cells which is very low. The action is quite similar to that of a steam-boiler safety valve by which steam is confined until the pressure rises to a certain value, when the valve opens and the steam escapes freely. When normal pressure is again reached, the valve closes. While the leakage current is only a few milliamperes, the plate area of the cells is ample to discharge lightning disturbances. The cells are provided with a fuse in series (600- and 1,500-volt designs) and a balancing resistance in multiple. The latter divides the line voltage equally across the cells. Evaporation of the electrolyte is prevented by a layer of oil on its surface.

When properly designed, the aluminum electrolytic arrester may be used for a.c. lines. It consists of a series of aluminum cones arranged in stacks separated by spacers of insulating material. The space between the cones is filled with electrolyte, so that the cells are thus arranged in series, each cone being bipolar. Inasmuch as the arrester would serve as a condenser and permit a substantial flow of current to ground if it were directly connected, it is commonly connected to the line through

a spark gap.   With a voltage high enough to jump the gap, the arrester can function.   The films tend to dissolve while the arrester is idle, so that these are commonly re-formed daily by drawing an arc across the gap and subjecting the cells to normal operating voltage for a short period.

Like ordinary static condensers, the electrolytic form consists of two conducting surfaces separated by an insulator, the latter being the high-resistance film on the conducting metal support. The cathode in the electrolytic cell is only an electrical contact. The actual thickness of film is from 0.001 to 0.00001 mm.[7]   With aluminum electrolytic condensers, large capacities per unit area may be obtained.

Dry Rectifiers.   The Cu-Cu_2O rectifier has been reviewed by Grondahl.[8]   Basically it is made of a disk or sheet of copper oxidized on one or both sides with a tightly adhering layer of cuprous oxide, with a contact to the "mother" copper and another to the oxide.   In an electric circuit such a unit will pass current more freely from the Cu_2O to the Cu than in the reverse direction from the Cu to the Cu_2O.   The relative resistances are a function of the applied voltage.   In simple laboratory types, the resistance ratios of Cu_2O to Cu compared to Cu to Cu_2O are of the order of 1:3, but Smith[9] states that in practice the ratios may be as high as 1:10,000.   The copper must be very pure, precleaning in advance of the formation of the Cu_2O layer is important, and CuO must be practically absent.   Typical construction of the disk type is shown in Fig. 51 and of the larger capacity, plate type in Fig. 52, while efficiencies of electroplating rectifiers are shown in Fig. 53.

Grondahl[10] states that the rectifier capacities, if sufficient ventilation be provided, are as high as several amperes per square inch at voltages below six, although special layers may rectify up to 30 volts.

Tone[11] states that SiC in the form of columns of granules in a

[7] SUTTON, H., and WILLSTROP, J. W. W., *Engineering*, **124,** 442 (1927); SIEGMUND, H. O., *Trans. Am. Electrochem. Soc.*, **53,** 203 (1928); SLEPIAN, J., *ibid.*, **54,** 20 (1928); ZIMMERMAN, C. I., *ibid.*, **7,** 309 (1905).

[8] GRONDAHL, L. O., *Trans. Electrochem. Soc.*, **72,** 225 (1937).

[9] SMITH, I. R., *Metal Cleaning Finishing*, **10,** 10 (1938).

[10] GRONDAHL, *Loc. cit.*

[11] TONE, F. J., *Chem. Inds.*, **45,** 137 (1939).

chamber of insulating material is an effective lightning arrester. Such forms of SiC rapidly decrease in resistance as the applied voltage increases, enabling the apparatus to discharge higher than normal voltage surges.
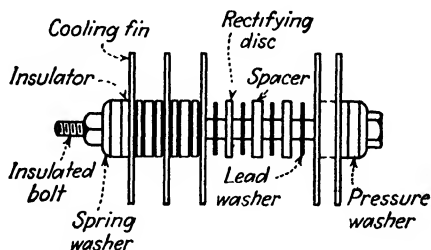
FIG. 51.   Disk type of copper oxide rectifier.
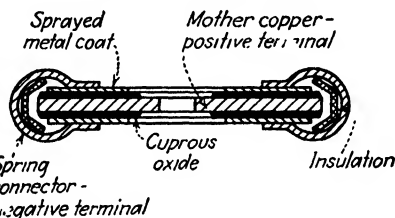
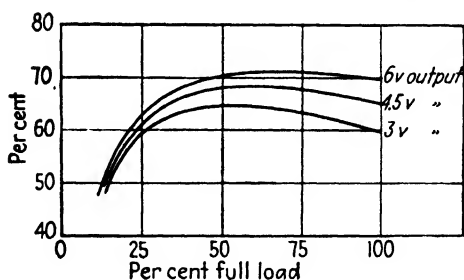FIG. 52.   Cross section of plate type of copper oxide rectifier.

FIG. 53.   Efficiency of plate type of copper oxide rectifier.

Selenium Rectifiers.   The selenium rectifier is a device for converting alternating current into direct current.[12]   It does so by virtue of the fact that it possesses electrical asymmetry,

[12] The selenium rectifier was first introduced on a commercial scale in Germany in 1928.   The International Development Co., Inc., now Federal Telephone and Radio Corp. (an International Telephone and Telegraph associate), first introduced it in the United States in 1938, and manufacture began in 1939.

allowing the current to flow more readily in one direction (termed "forward") than in the other (termed "reverse").

The selenium rectifier possesses nonohmic characteristics so that both the forward and the reverse resistances are voltage dependent. These characteristics also vary with time: in the forward direction, the irreversible changes associated with an increased resistance are known as "aging"; in the reverse direction, the reversible changes encountered are termed "creep."
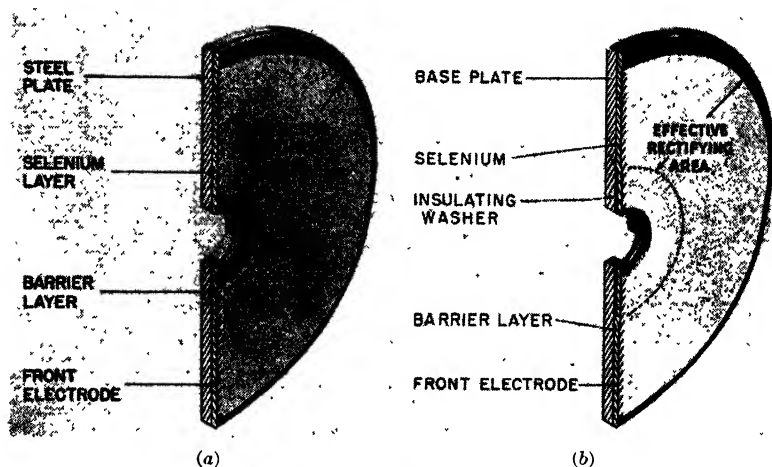
Fig. 54. Cross-sectional views of (a) petal-contact and (b) center-contact rectifier plates, respectively. (*Federal Telephone and Radio Corporation.*)

Finally, the reverse resistance will display either a positive or a negative temperature coefficient as a function of both temperature and voltage.

The rectifier consists essentially of a layer of selenium sandwiched between two metallic layers. One of these, the base plate, usually made of steel or aluminum, acts as the carrier or support of the selenium layer and as one of the electrodes; the other, the front or counterelectrode, usually made of a low-melting-point alloy such as Wood's metal, provides the so-called "barrier" layer at the selenium-counterelectrode interface and acts as the other contact to the external circuit.

Figures 54a and 54b are cross-sectional views of a selenium rectifier plate of the "petal-contact" and "center-contact" types, respectively. In normal construction no counterelectrode is applied to the central portion of petal-contact plates so that

pressure can be applied in assembling the plates into stacks without affecting the reverse resistance of the rectifier. Electrical connection to the counterelectrode is made by means of a spring brass disk (petal) with an insulating washer mounted under the spring contactor and over the unsprayed central portion of the rectifier plate (see Fig. 55a).

The center-contact plate, on the other hand, employs a thin nonconducting washer around the center hole of the base plate

(a)   (b)
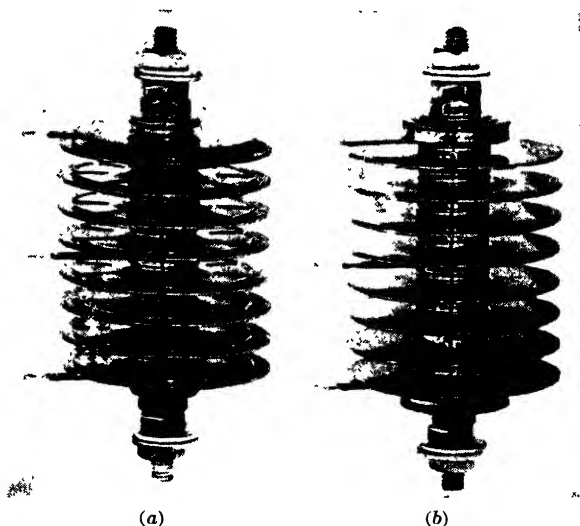
Fig. 55. Typical selenium rectifier using (a) petal-contact and (b) center-contact assemblies, respectively. (*Federal Telephone and Radio Corporation.*)

before the selenium is applied, in order to insulate the base plate from the selenium. Such plates with center-contact construction can be assembled into a stack such as shown in Fig. 55b, and assembly pressure can be applied without fear of damaging the rectifiers. Such a stack also allows slightly better cooling and has the advantage that it can be easily and effectively dipped into paints and varnishes without fear of breaking any electrical connections.

Positive current flows readily from the base plate to the counterelectrode but practically not at all in the opposite direction. The reverse considerations hold true for the flow of electrons. Each plate, therefore, performs as a half-wave rectifier. In order to obtain full-wave rectification, two or more plates

must be connected in one of the conventional single- or three-phase circuits (see Fig. 56).

The so-called barrier or blocking layer represents an electrical state of affairs at the selenium-counterelectrode junction. By

Circuit	Single phase half wave	Single phase center tap	Single phase bridge
Rectifier connection			
Resistive load Approximate output voltage wave shape			

Circuit	3 phase half wave	3 phase bridge	3 phase center tap
Rectifier connection			
Resistive load Approximate output voltage wave shape			
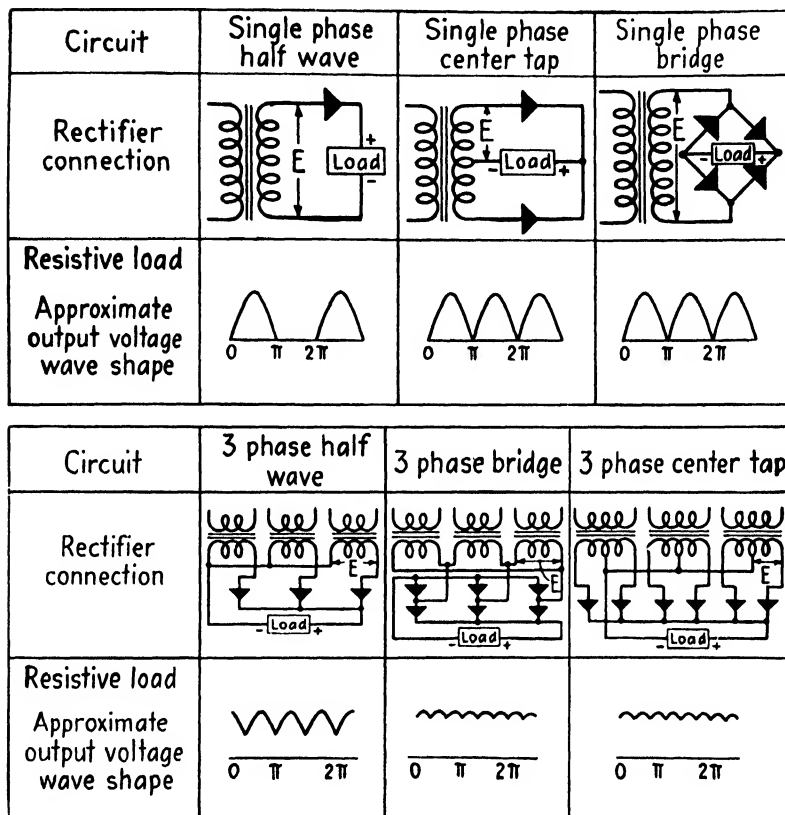
Fig. 56.   Basic characteristics of rectifier circuits.   (*Federal Telephone and Radio Corporation.*)

suitable chemical treatments of the selenium layer before application of the counterelectrode, it is possible to improve the blocking characteristics of the barrier layer without unduly increasing the electrical resistance in the conducting (forward) direction.   Escoffery[13] has described the manufacture of selenium rectifier units.

[13] Escoffery, C. A., *Trans. Electrochem. Soc.*, **90**, 129–162 (1946).

Part III

ELECTROLYTICS

CHAPTER 13

METAL DEPOSITION AND SOLUTION

Industrial metal deposition processes fall into three general classes, each of which has differing requirements for the physical condition of the cathode product. In electroplating, a fine-grained, tenacious, strongly adherent, bright or readily polishable layer of crystals is necessary. In refining, relatively large-grained, coarse, but adherent deposits are satisfactory. These must be of high purity and of sufficient strength to stand ordinary handling in advance of the usual melting and casting into shapes for further working. In the production of metal powders in the electrolytic cell, controlled grain size of product is needed, but nonadherence or poor adherence to the cathode is a desideratum. In general, powder production calls for the antithetical conditions to those of electroplating. In some phases of powder manufacture, noncohering slimes of poor cathode adhesion are favorable to the production of material of desired specifications.

In plating, efficient utilization of electrical energy is decidedly secondary to the quality of the plating. While high current and energy efficiencies are desirable, they may be sacrificed without upsetting the economic phases of the operation. In refining, particularly where thermal or chemical processes compete, power cost is a very important item; maximum current and energy efficiencies are vital to the economic justification of the method. In metal powder production, conditions approach refining to a far greater degree than plating, as the procedures compete with thermal and mechanical methods.

Cathodically deposited metal may vary in its characteristics over a wide range, depending upon the electrolyte itself, with particular reference to the ions present. Silver when deposited from a solution of $AgNO_3$ forms large, readily visible crystals. Tin deposited from a solution of $SnCl_2$ will form long needles which may rapidly "bridge" from the anode to the cathode. The deposits of lead from a chloride or acetate solution are

markedly different from those produced when a chlorate or perchlorate is the anion. Nickel from a sulfate bath may give hard deposits which may be polished but not with ease, while from a naphthalene sulfonate bright deposits which need little if any polishing may be produced.

The character of the electrolyte, the pH of the solution, the metallic ion concentration, the anodic and cathodic current density, the temperature of the electrolyte, the simplicity or complexity of the metallic ion including its primary and secondary ionization, as well as the presence of modifying or "addition" agents, all have their effect on the character of the deposit. Some interesting work has been done on the "titration of characteristics" of electrolytes, in which case baths giving somewhat slimy, dull, but adherent deposits have been added to others giving highly crystalline metallic forms, in such proportions as to produce an electrolyte from which solid metal of satisfactory characteristics was obtained.

In their discussion of the form of electrodeposited metals, Blum and Rawdon[1] conclude that the cathode discharge of metal ions and the formation of crystals constitute one and the same process. Any given ion is discharged at the point where the lowest discharge potential is needed. This discharge potential is a function of the solution pressure of the metal and the effective metal ion concentration adjacent to it. As further postulates of their theory, Blum and Rawdon hold that

The single potential and solution pressure of a metal are the resultant of (1) the "primary single potential," which is defined in terms of the solution pressure of a single unoriented atom, and (2) the "orientation potential," which is a measure of the diminution in solution pressure and corresponding algebraic increase in single potential caused by the arrangement or orientation of the adjacent metal atoms. A higher potential is required to discharge an ion in a position unrelated to those of previously discharged atoms (that is, to form a nucleus) than upon an existing crystal, and similarly a higher potential is required to discharge an ion upon a small crystal than upon a large crystal.

The crystalline structures of cathode deposits are classified as follows:

Group I. All (or practically all) the initial nuclei or crystals continue to grow throughout the deposit.

[1] RAWDON, H. S., *Trans. Am. Electrochem. Soc.*, **44**, 397 (1923).

1. Isolated crystals:
    a. Symmetrical
    b. Acicular
2. Contiguous crystals:
    a. Columnar
    b. Fibrous

Group II.   Only part of the initial nuclei or crystals continue to grow.
    1. Conical ("normal")
    2. Twinned

Group III.   No crystals continue to grow for any extended period.
    1. Broken (compact)
    2. Arboreal ("treed")
    3. Powdery (spongy)

Lewis and Lacy[2] observed that the solution pressure and single potential of a metal vary with the state of division. Crystal growth consists first of the formation of nuclei or minute new crystals followed by the growth of existing crystals. Any conditions that increase the rate of formation of nuclei tend to increase the number of crystals, and opposing conditions inhibit the increase. Under rather specific conditions, Rosa, Vinal, and McDaniel[3] found that the number of nuclei are increased with increases in current density, with decrease in metallic ion and metallic salt concentration, and decrease of temperature. Aten and Boerlage[4] found that the number of crystal nuclei increased if any addition were made to the solution which would increase the cathode polarization. The current densities are increased, and the effective metal ion is decreased in the solution adjacent to the cathode by

1. Diluting the solution
2. Decreasing the temperature, thus reducing diffusion and convection
3. Adding a salt with a common ion
4. Introducing a colloid addition agent
5. Increasing the viscosity of the solution
6. Forming of complex ions

These increase the cathode potential difference and the number of crystal nuclei. These factors all tend toward the production of fine-grained deposits.

[2] LEWIS, G. N., and LACY, W. N., *J. Am. Chem. Soc.*, **36**, 804 (1914).

[3] ROSA, E. B., VINAL, G. W., and McDANIEL, A. S., *Natl. Bur. Standards (U.S.) Sci. Paper* 195, 1912.

[4] ATEN, A. H. W., and BOERLAGE, L., *Rec. trav. chim.*, **39**, 720 (1920).

Replenishment of metal ion concentration, particularly at the surface of the cathode, is affected by dissociation, ionic migration, diffusion, and convection.   The growth of existing crystals may be fostered by acceleration of these factors and hindered by retarding them.   The tendency of metals like silver and lead deposited from nitrate solut ons to form isolated crystals is partly due to the relatively large change in density of the solution produced by the removal of the metal.   The effects of various factors upon the structure of deposits are summarized in Table 27.

TABLE 27.   DIRECTION OF EFFECTS UPON STRUCTURE OF DEPOSITS

Change in Operating Condition	Change in Structure Group
Increase metal salt concentration..... ...	III → II → I
Increase metal ion concentration.	III → II → I
Agitate solution....	III → II → I
Elevate temperature...	III → II → I
Increase conductivity of solution...........	III → II → I
Add colloids to solution	I → II → III
Increase viscosity of solution.......... .. .	I → II → III
Increase current density . ..	I → II → III

Decreasing the metal ion concentration decreases the size of the crystals.   Fine-grained, bright, or hard deposits are produced at low temperatures, while increase of temperature causes coarse or soft deposits.   The effects of increases of current density and temperature are in opposite directions.   It is therefore possible to obtain fine-grained deposits in warm solutions at a high current density as well as in cold solutions with a lower current density.   Additions of colloids in more than small amounts, increases of viscosity, and increases in current density tend in the direction of broken crystals, arboreal, or powdery forms of electrolytically precipitated material.

Temperature.   Increases of temperature ordinarily increase the conductivity of the electrolyte as well as increase diffusion rates, chemical solution at the anode, and re-solution at the cathode.   The over-all net effect is a decrease of polarization and a lowering of the cell voltage.   Increase of temperature stimulates crystal growth rather than encouraging the formation of new nuclei.   Lowered resistivity of the electrolyte with increased temperature causes lessened current concentration at protruding points on the cathode, so that irregularities develop less rapidly than at lower temperatures.   When polarization varies directly

with current density, inasmuch as increase of temperature reduces this polarization, nodule formation may be favored by higher temperatures in that higher current density may be employed for the same polarization value. Hydrogen evolution and precipitation of oxides are lessened through the reduction of the polarization and their effect on the character of the deposit decreased. Base metals of high hydrogen overvoltage, like zinc, act in an opposite manner. Temperature increase promotes hydrogen evolution and the precipitation of contaminating salts. Both these factors deleteriously affect the character of the deposit.

Current Density. Increasing the current density of the cell, in that the current per unit of area of electrode surface is intensified, augments the capacity or output of products and decreases capital cost, floor space per unit of product, and interest charges on material in operation. Upward changes in current density cause cell voltages and contact losses to rise, while energy efficiencies are lowered. In most electroplating operations, the range of current density is limited, in that the physical character of the deposit is the controlling factor.

For any given process, the most desirable current density results from a balance of many factors, such as power cost, operating charges, value of material in process, and energy consumption per unit of product. In materials as valuable as gold undergoing refining, high current densities are employed even though they be less efficient, to speed the valuable product through the operation and minimize high interest charges.

Conductivity. In many baths additions of salts, acids, or bases are made to lower the resistance of the electrolyte. The potential drop through the electrolyte itself is lowered for the same current density. It is not possible to change the conductivity of a solution without changing some other properties such as the metal ion concentration. The addition of H_2SO_4 to a $CuSO_4$ solution increases the conductivity, but the common ion effect decreases the Cu^{++} ion concentration. Inasmuch as the increase in conductivity produced by the H_2SO_4 is many times greater than the decrease in metal ion concentration, the assumption is made that better performance is due to the lowered resistance.

Throwing Power. Throwing power may be defined as that property of a solution by virtue of which relatively uniform

distribution of metal is obtained upon a cathode of irregular shape.[5] It may also be defined as the deviation of the actual metal distribution from the primary current distribution. Haring and Blum[5] by mathematical and experimental means have shown that throwing power is dependent upon the rate of change of cathode potential with current density, the resistivity of the solution, and the cathode efficiency at various current densities. They devised a mechanism for measuring under definite and reproducible conditions the metal distribution upon two plates at the same potential with respect to each other but situated at different distances from the anode. Pan[6] proposed the term "throwing efficiency" as a value indicating the extent to which the throwing power approached a unity value.

These factors are of importance in electroplating and electroforming. The primary current distribution is determined by the dimensions of the electrode and of the electrolyte. It is realized only when there is no polarization at the cathode or the polarization is equal on all parts of the cathode, or when alternating current of sufficient frequency is applied to reduce any polarization tendency to a minimum. The actual or secondary current distribution is a function of the composition of the electrolyte. The distribution of metal on a cathode is determined by the secondary current distribution and the cathode current efficiency. Mathematically, throwing power may be computed from the cathode single potentials, the conductivity of the solution, and the current efficiencies.

Metal Ion Concentration. The metal ion concentration in an electrolyte is affected by the molal concentration of the salts, their ionization (which in turn is affected by the molal concentration), the temperature, the presence or absence of common ions or of bath constituents with which complex ions are formed (which in turn give rise to metal ions not by primary but by secondary processes). Additions of common ions produce only a relatively slight change in metal concentrations, particularly in concentrated solutions, as the result of the limited solubilities of the salts which might be added. Formation of stable complex ions markedly reduces the metal ion concentration. Very low

---

[5] HARING, H. E., and BLUM, W., *Trans. Am. Electrochem. Soc.*, **44,** 313 (1923).

[6] PAN, L. C., *Trans. Am. Electrochem. Soc.*, **58,** 423 (1930).

molal concentrations yield powdery deposits even at low current density.

Of the complex ions, those of the "double cyanides" are favored for the plating of metals such as silver, copper, cadmium, zinc, and brass. Metal ion concentration is low as the result of secondary ionization, while the primary ions serve as a reservoir from which a small but constant supply of material available for crystal growth is furnished.

pH. The pH of an electrolyte from which metal is deposited markedly affects both the character and appearance of the deposit as well as the current efficiency. In some industrial processes such as nickel, buffers such as boric acid are added to maintain the pH at a desired point. In nickel plating different operating conditions are necessary if the process be carried on near the neutral point or at low pH under condi⋅'ons of relatively greater acidity. In iron deposition the acidity of the bath may be such that there will be chemical dissolution of the deposit whose rate may exceed that of electrolytic deposition. In a somewhat analogous man ner the pH of the bath may be so high, *i.e.*, so alkaline, that similar dissolution effects are encountered under poor operating conditions. In electrowinning operations, as the electrolyte is depleted of metal, the pH increases so that deposition occurs over a wide range of conditions. Decrease in pH, *i.e.*, increase in acidity, favorably affects the conductivity and increases the deposition polarization. The precipitation of basic salts is prevented, but hydrogen evolution is favored.

Addition Agents. A wide range of colloidal or reducible substances have been added to electrolytes to improve the quality of the deposit. Bancroft[7] stated that crystal size is decreased when there are present at the cathode surface substances which are adsorbed by the deposited metal. A wide range of high-molecular-weight organic products have been found to give smoother and finer grained deposits in particular cases.[8] Substances which increase the weight of the cathode deposit, *i.e.*, are adsorbed, tend to reduce the size of the crystals in the deposit, whereas substances which do not vary the crystal size

[7] BANCROFT, W. D., *Trans. Am. Electro.hem. Soc.*, **6**, 27 (1904); **23**, 266 (1913); *J. Phys. Chem.*, **9**, 277 (1905).

[8] MATHERS, F. C., *Trans. Am. Electrochem. Soc.*, **21**, 313 (1912); **24**, 315 (1913); **26**, 99 (1914); **31**, 271 (1917); FRÖLICH, P. K., CLARK, G. L., and

cause no increase in the weight of the deposit for the same amount of current.

Metallic ion additions affect the character of deposits. They are often referred to as brighteners, an example of which is the addition of nickel, cobalt, or copper salts to cadmium electrolytes.[9] Addition agents such as glue in copper and lead refining, or reducible sugars in cadmium and tin plating are common.

Anodic Metal Solution. Anodic solution of a metal in an electrolyte of its own ions takes place almost reversibly with the development of some concentration polarization in the films adjacent to the anode. When the electrolyte is such that the metal ion exists in complex form, even at moderate current density, some polarization exists. The amount of this polarization varies with different metals. The formation of anode films and the onset of passivity are factors which increase this polarization necessary for the continuance of anode solution. In industrial operations, substances termed "anode corroding agents" are present or are added. Chlorides are effective in this regard and are found in nickel-refining and nickel-plating solutions to overcome the tendency of the metal toward passivity. Formerly nickel electroplating anodes contained an appreciable amount of carbon and as a result were impure. Later the effect of small amounts of sulfur as a depolarizing agent was utilized to advantage in the preparation of nickel anodes. In industrial processes it is seldom that pure metals are employed as anodes; in refining operations the composition of the anode is quite complex.

The metals of the iron group tend to depolarize the OH^- ion discharge. "Oxygen alloys" may be formed at potentials lower than that required for oxygen evolution, and the anodic solution of the metal may be retarded. This may continue so that potentials are reached at which there is a cessation of metal solution, and oxygen evolution takes place. The anode is then "insoluble" and passive.

ABORN, R. H., *ibid.*, **49,** 369 (1926); VUILLEUMIER, E. A., *ibid.*, **50,** 229 (1926); FUSEYA, G., and MURATA, K., *ibid.*, **50,** 235 (1926); FUSEYA, G., and NAGANO, M., *ibid.*, **52,** 249 (1927); WESTBROOK, L. R., *ibid.*, **55,** 333 (1929); KERN, E. F., and ROWEN, R. W., *ibid.*, **56,** 379 (1929); KERN, E. F., and JONES, T. R., *ibid.*, **57,** 255 (1930).

[9] WESTBROOK, L. R., *Trans. Am. Electrochem. Soc.*, **55,** 333 (1929).

In the case of the so-called "insoluble anodes," the anode material may act as a catalyst for the oxygen evolution reaction, with resultant decrease in anodic solution of the material. Noble metals such as gold show anodic solution only within a very limited range, whereas platinum and related metals under most circumstances behave as practically insoluble anodes. The passivity of metals is of considerable industrial importance and is discussed further under electrolytic corrosion and in connection with the commercial application of insoluble anodes.

The previous mechanical and thermal history of the metal employed as an anode is often of great importance. Operations such as rolling, hammering, welding, drawing, or deforming as well as heat-treatment, cause increased electrolytic solution pressures to exist. Metals in a state of strain will have more negative electrolytic potential values than those normal for the metal. The differences, however, are usually small. Metals used as anodes in any case are never free from local differences in structure. They will often show small differences in electrolytic potentials at various parts of their surfaces. The baser portions of the anode will dissolve first. Often undissolved or insoluble particles will fall off and become slimes at the bottom of the tank, or else remain in suspension in the solution. Considerable differences in practice are often observed in the action of rolled or hammered metal as contrasted with cast material. This topic will be discussed in greater detail under electrolytic refining.

In general, the more negative metal or compound at the surface of the anode will dissolve first. When this is all used up and the electrolyte does not have access to underlying portions because they are covered by the other components, the next most negative compound or metal will dissolve at an electrode potential corresponding to the new process. The more negative material may be removed from the neighborhood of more positive metals or compounds and so loosen it that it becomes detached from the body of the anode, falling to the bottom of the tank to become part of the anode mud.

In electrolytic metal refining, high current densities are used so that anode potentials are greater than their equilibrium value. Constituents ordinarily insoluble may dissolve under these conditions. Adhering layers may coat the electrode, interfering

with metal solution and affecting polarization to an extent that these values may be raised and the coating itself be caused to go into solution. If, however, the slimes readily detach themselves and drop from the anode, disturbances such as those described may not occur. The crude anodes containing only a few per cent of impurities, which in turn consist not of one metal but of several, favor effective electrolytic refining. Complex alloys consisting of solid solutions of many constituents dissolve less readily than simple binary or ternary forms.

Anode Film Formation. If the metal ions pass into an electrolyte containing anions which precipitate out to form insoluble or slightly soluble substances, coatings or films may form over the anode. If, however, the electrolyte contain constituents which dissolve the normally insoluble material, anode solution will continue. In a chloride electrolyte a lead anode tends to become coated with insoluble $PbCl_2$, but if the electrolyte contain a sufficient quantity of NaCl in which $PbCl_2$ is soluble, anode solution will proceed. On the other hand, in the case of the lead-silver alloys proposed for chlorine electrolysis,[10] consisting of 61 per cent Ag and 39 per cent Pb by weight, the insolubility of the anode is a function of the strongly adhering insoluble silver chloride-lead peroxide film. Film formation on aluminum anodes is the basis of "anodizing," discussed in connection with electroplating, which produces corrosion-resistant coatings on aluminum and its alloys. The effect of film formation in rectification has been discussed elsewhere.

Anodic solution of the metal is modified by the formation of films, as a result of the electrical resistance, porosity, and physical character of the film. The coatings reduce the effective electrode surface and increase the current density at the remaining areas. This, in turn, causes voltage or polarization effects and the onset of new electrode processes. If the film be of high resistance and low porosity, metallic ion solution will cease. If, however, the coating be of low resistance and high porosity, anions may migrate through the film and discharge at its surface.

When precipitates which would otherwise coat the electrode are caused to form at some distance from the electrode as the result of diaphragms or electrolyte flow, the basic conditions involved in electrolytic pigments are established. If lead be

[10] FINK, C. G., and PAN, L. C., *Trans. Am. Electrochem. Soc.*, **49**, 85 (1926).

electrolyzed in dilute H_2SO_4, insoluble $PbSO_4$ films which are poor conductors soon coat the anode. Current density and potential rise. A new electrode process, that of tetravalent lead-ion formation, may set in. The $PbSO_4$ may hydrolyze and give rise to the formation of PbO_2, which is then deposited on the anode. This has good adherence and is a good conductor, and effectively converts the electrode into an insoluble PbO_2 material at which there is no anodic metal solution but only oxygen evolution. If chlorates be present[11] in the electrolyte in sufficient quantity, soluble lead salts will be formed, which in turn will be precipitated as $PbSO_4$ at some distance from the anode, and anodic metal solution will continue. A somewhat similar set of conditions is used in the production of electrolytic white lead and lead pigment, which are discussed from the industrial viewpoint elsewhere in this volume.

Müller[12] found that bismuth and antimony behave in a manner similar to lead in H_2SO_4 solutions. Tin gives stannous ions and a film of SnS in sodium sulfide electrolytes.[13] The film causes potential increases so that stannic ions, which form SnS_2 soluble in the electrolyte, are produced as the result of the major anode reaction.

Passivity. Metal solution at the anode may, without noticeable film formation, be obstructed by or replaced by anion discharge. Metals of the iron group and chromium require high polarization for anodic solution and are readily rendered passive. The metal acts as if it were rendered insoluble or were ennobled, behaving like platinum and gold. The reversible potentials of these metals are close to those necessary for oxygen evolution. Tin shows passivity in alkaline solutions. Foerster and Dolch[14] showed that this condition could be removed by mechanical abrasion of the anode. Schoch[15] found that the current density at which the electrodes become passivated was affected by the

[11] LUCKOW, C., *Z. Elektrochem.*, **3**, 482 (1897); LEBLANC, M., and BINDSCHEDLER, E., *ibid.*, **8**, 255 (1902); ISENBURG, A., *ibid.*, **9**, 275 (1903); JUST, G., *ibid.*, **9**, 547 (1903); JUST, G., ASKENASY, P., and MITROFANOFF, B., *ibid.*, **15**, 872 (1909); FISCHER, F., *ibid.*, **16**, 355 (1910); SCHLEICHER, G., *ibid.*, **17**, 554 (1911).

[12] MÜLLER, W., *Z. Elektrochem.*, **15**, 696 (1909).

[13] WOLF, J., *Z. Elektrochem.*, **13**, 209 (1907); **15**, 236 (1909).

[14] FOERSTER, F., and DOLCH, M., *Z. Elektrochem.*, **16**, 599 (1910).

[15] SCHOCH, E. P., *Trans. Faraday Soc.*, **9**, 275 (1914).

anions in the electrolyte. Halides, mentioned previously as an anode corroding agent in industrial processes, tend to prevent passivity; oxidizing agents may induce it.

Considerable study has been devoted to regulation of current density at an electrode which may be made alternately passive and active, assuming such states in a cyclic fashion.[16] The superposition of alternating current to eliminate or reduce passivity in connection with noble metals such as gold is employed in the Wohlwill refining process. Chromium is readily rendered passive, particularly in electrolytes such as chromic acid. This condition sets in so readily that processes for chromium plating are unable to operate with chromium anodes as a source of metal for deposition at the cathode.

The question of passivity in connection with individual metals has been much studied[17] and many theories have been proposed.[18]

[16] ADLER, A., *Z. physik. Chem.*, **80**, 385 (1912); Sammlung, *Chem. Vorträge*, **19**, 289 (1913); SMITS, A., and LOBRY DE BRUYN, C. A., *Proc. Acad. Sci. Amsterdam*, **21**, 382 (1919); McCULLOCH, L., *Trans. Am. Electrochem. Soc.*, **50**, 379 (1926); **56**, 325 (1929).

[17] FOERSTER, F., "Elektrochemie wässeriger Lösungen," pp. 415–429, J. A. Barth, Leipzig, 1923.

[18] *Trans. Faraday Soc.*, **9**, 203–290 (1914); **19**, 748 (1924); ASTON, J., *Trans. Am. Electrochem. Soc.*, **29**, 449 (1916); BENNETT, C. W., and BURNHAM, W. S., *J. Phys. Chem.*, **21**, 107 (1917); BANCROFT, W. D., *ibid.*, **38**, 785 (1925); EVANS, U. R., *Ind. Eng. Chem.*, **17**, 363 (1925); BAYLIS, J. R., *ibid.*, **18**, 370 (1926); WHITMAN, W. G., *Chem. Rev.*, **2**, 421 (1926).

CHAPTER 14

ELECTROPLATING AND ELECTROFORMING

Electroplating concerns itself with the production of metallic coatings on metal objects and to a limited extent on nonmetallic articles. These coatings are very thin layers of some other metal or metals over the original surface of the object. The plating may be applied for decorative purposes and after application may be given various chemical and electrochemical treatments with the resultant production of different colored "finishes." The plating may be deposited for the purpose of improving the corrosion resistance of the base metal and lengthening its industrial life. In many cases platings are made for combinations of these purposes. Electroplating operations allow the use of relatively cheap metals from which the object may be fabricated, these base materials being coated with a layer or layers of other metals to improve their appearance and increase their ability to withstand the destructive influence of the atmosphere and industrial conditions. A special modification of electroplating concerns itself with the application of metallic coatings on articles which are worn or damaged, in which case relatively thick layers of metal are built up on these pieces. In still other cases objects such as gages may be manufactured so that their dimensions are smaller than those of the finished article, and the object plated to its final dimensions, the covering being of a harder and more resistant material than the main body of the article. Chromium has found particular application in this connection.

In general the metal to be deposited is dissolved from an anode of the material immersed in an electrolyte containing ions of the metal which are discharged on the object being plated as cathode. This arrangement may be modified and an insoluble anode used, the metal being plated from a dissolved salt in the plating bath. Where soluble anodes are used, the electrochemical action at the cathode is the reverse of that at the anode. The

223

emf applied at the terminals of the bath is used to overcome the ohmic resistance of anodes, cathodes, connectors, the external circuit, the various contact resistances, the resistance of the bath itself, the voltage drops through the films adjacent to the anode and cathode, and concentration polarizations at these points, plus other polarizations for the deposition of the metal in question and the difference between the anodic solution and the cathodic deposition potentials of the metallic ion in question. In the case of insoluble anodes where oxygen may be evolved, the anodic solution potential of the metal is eliminated and the overvoltage of oxygen as well as the decomposition voltage of the electrolyte become important factors. In general the terminal emf of a plating tank is low. Electroplating generators are built to supply either 6- or 12-volt high-amperage current.

Preparation of Articles for Plating. Preparation of articles for plating is as important as the plating itself for the production of high-quality finishes of impervious adherent metal coatings. It is of greatest importance that the article to be plated be thoroughly cleaned. Foreign materials likely to adhere to metallic surfaces are of two kinds: (1) oxides or related products of corrosive influences, such as scale, tarnish, or rust; and (2) organic substances such as grease, oil, and various forms of dirt. In general, if the grease and corrosion products be removed, other foreign substances will also be eliminated. Generally the corrosion products are oxides removable either by mechanical abrasion or by pickling, involving solution in acids. In the latter case grease must be removed first so that uniform action of the pickling acid may be obtained. No general statement can be made as to methods applicable to the preparation of articles for plating, in that a large number of factors need to be taken into account. Some of these are the material of the object and its condition, shape, size, composition, and surface appearance. Ordinarily the plating will exactly follow the contours of the object to be plated. Smooth finishes can be produced only on smooth surface objects. Rough surfaces can be treated mechanically by sandblasting, steel-wire brushing, grinding, and "cutting down" with abrasives. Some removal of the roughness of the object may be accomplished by pickling, generally with H_2SO_4 or occasionally in HCl or other acid solutions. The chemistry of pickling in recent years has received much study,

and considerable attention has been paid to the factors involved in equipment for large-scale operation.

Grease, oil, dirt, and lacquers are removed by some form of alkaline cleaner, often containing oxide solvents such as cyanides, and detergents such as Na_3PO_4, as well as other materials.
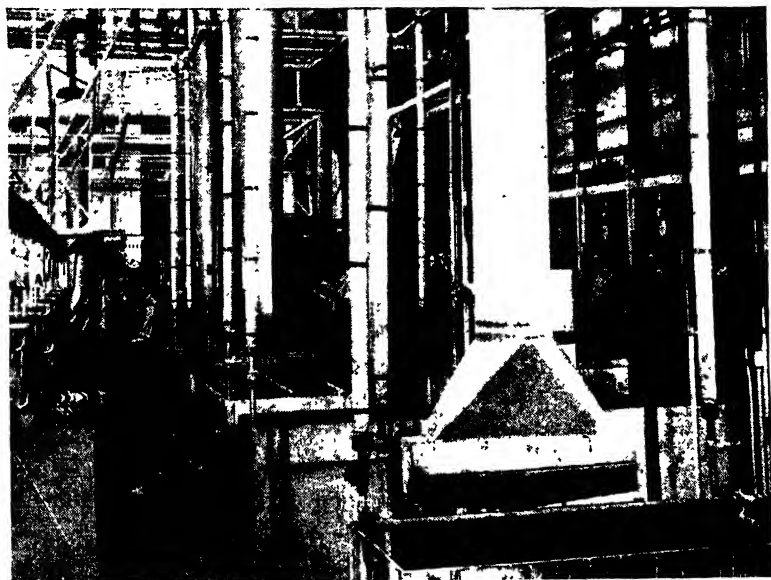
Fig. 57.   Chromium plating in an automotive plant.   (*The Iron Age.*)

These may be operated alone or with the aid of the electric current in which case the object is suspended in the cleaning solution from a rod and is made cathode, or in other cases alternately anode and cathode in the circuit.   At other times grease and dirt may be removed by organic solvents, usually of the petroleum type.   In some cases after cleaning, the object may be further pickled or else may receive additional mechanical surfacing treatment for the production of preliminary polishes. In the case of nonferrous articles, pickling is ordinarily done in so-called "bright" acid dips consisting of mixtures of concentrated H_2SO_4 and HNO_3 with the addition of small amounts of salt.   Depending upon the object and the type of surface to be produced on the article, the preliminary flow sheet may vary widely in different industries.   In order to avoid contamination of solutions, one by the other, as a result of the material being

carried over when articles are transferred, and the introduction of acids into cyanide plating baths or vice versa, all operations irrespective of their nature are followed by washing or rinsing.

FIG. 58. Automatic nickel plating. (*The Iron Age*.)

Electrolytic Cleaning. In electrolytic cleaning, solutions containing a fairly high content of alkali are employed as electrolyte. Alkaline salts such as Na_3PO_4 or Na_2CO_3 are added to control the alkalinity of the solution and aid in emulsifying "dirt." Iron anodes or, more frequently, the iron tanks are used as anodes, the object to be cleaned being hung on the cathode bar. Sufficiently high emf is applied so that a current density of at least 10 amp per sq ft (1 amp per dm^2) is obtained on the cathode, at which a vigorous evolution of gas occurs. Cleaning takes place rapidly, partly as the result of the formation of free alkali at the cathode, but also because of the mechanical action of the hydrogen which is evolved on the metal surface and tends to lift off films of oil, grease, paint, and dirt, and to assist in their emulsification. The gas evolution causes agitation of the solution and hence constantly brings fresh portions of the bath to the cathode surface. When zinc, tin, lead, or their alloys are cleaned electrolytically, there is a tendency for them to dissolve

in the alkaline solution and be redeposited in small amounts in thin films. These films may prevent adherence of electroplatings. Under such conditions the redeposited metal is removed by causing the piece to function as anode for a short time. Electrolytic cleaning has been applied industrially in operations not connected with electroplating, such as the removal of paint from paint cans so that they may be reused, cleaning of steel barrels, drums, and shipping containers.

Electrolytic Pickling. Electrolytic pickling has found commercial employment, particularly for the removal of oxides on machined parts which have been heat treated. The operation is analogous to electrolytic cleaning in that the object to be pickled is hung on the cathode rod and suspended in an acid electrolyte containing chiefly H_2SO_4. Operating temperatures vary from room temperatures to those near the boiling point, depending upon the object treated. Sufficiently high current density is applied so that hydrogen is copiously evolved at the cathode. The hydrogen in expanding pries off the scale bit by bit and bubbles to the surface. Lead anodes are commonly used. If the electrolyte contain chlorides as the result of addition of either HCl or NaCl, the anode will be attacked and a thin layer of lead deposited on the object being pickled. Experimental tests do not indicate any striking advantage of the electrolytic over chemical pickling methods as far as the amount of acid used is concerned, but it is possible to employ lower temperatures and obtain better surfaces with electrolytic pickling than by chemical methods. In the case of steel, the amount of iron dissolved by the two methods varies considerably with different kinds of scale. Electrolytic pickling in general is more rapid than chemical pickling.

Scale-removing methods have been devised which consist first of electrolytic pickling followed by electrolytic cleaning. In one method the object is hung as cathode in a lead- or rubber-lined tank with anodes of metals which form protective films on the object, such as lead which is commonly used, or tin and zinc. Electrolytic pickling is done in an electrolyte consisting of dilute H_2SO_4 and HCl and some NaCl at 65°C. Because of the presence of chlorides in the electrolyte and resultant anode corrosion, thin adherent metal films of lead are deposited on the object being pickled. This action continues until all the scale has been

removed and all the surface coated. At this time the object is removed from the acid bath and placed as anode in an electrolytic cleaner containing soda ash, caustic soda, and a small quantity of Na_3PO_4 at 90 to 100°C. In this bath the lead coating deposited in the acid bath is removed, after which the object is withdrawn, washed, and dried. The process is stated to be free from the difficulties of pickling and hydrogen embrittlement. It need not be very carefully controlled, inasmuch as in the acid bath, after the first layer has been deposited, further action results in the deposition of porous spongy deposits without detriment to the object.

Electrolytic Polishing. Madsen[1] noticed that concentrated acid solutions produced electrolytic etches having whiter surfaces than ordinbry etching at high current density. Electrolytic polishing involves the treatment of metallic surfaces in baths of sulfuric, phosphoric, chromic, or citric acids and to a lesser degree hydrofluoric, perchloric, and acetic acid or combinations of these, at high current density. In electrolytic polishing, the high spots are preferably dissolved (with the article as anode) under conditions between uniform corrosion (as in electrolytic pickling) and complete anode polarization (as in an insoluble anode). Passivation occurs in the valleys or low spots because anode corrosion products form poorly conducting viscous films which adhere, yet these films fall away at the high spots and allow corrosion to continue there. The high or projecting areas are reduced until their level is brought down to the low spots with the result that a polishing similar to that effected mechanically is achieved.

Electrolytic polishing is applied to the stainless steels and irons, nickel, aluminum, copper and its alloys, and electroplated silver. Operating conditions show current densities from 100 to 500 amp per sq ft and in the case of wire 5,600 to 6,000 amp per sq ft, at voltages of 3 to 15 and temperatures from 60 to 150°F. Application time is a function of current density and temperature. Approximately 0.001 in. of metal is dissolved in 10 min at 3C0 amp per sq ft. Cathodes are used only to complete the electrical circuit and so are made of materials resistant to the bath.

[1] MADSEN, CHARLES P., U.S. Patent 1,562,710 (1925).

Constituents of Plating Baths. Plating baths may be considered to consist of a number of different parts: (1) the salt or acid containing the metallic ion or radical; (2) if this salt be not sufficiently conductive, an additional salt whose function is to increase the conductivity of the bath; (3) if the metallic ion salt or acid does not so serve, a material to increase anode corrosion and prevent its passivity; (4) added materials termed "addition agents," employed in small amounts to affect the crystalline nature of the deposit; and (5) if the bath be operative successfully only over a narrow range of acidity, a buffer to maintain the proper pH of the solution. Some baths may contain all of these; others may not, in that one substance may have more than one function. For example, a common nickel-plating solution will have the metal ion in the shape of $NiSO_4 \cdot 7H_2O$, NH_4Cl or $(NH_4)_2SO_4$ to increase the conductivity of the bath, $NiCl_2 \cdot 6H_2O$ to assist anode corrosion, and H_3BO_3 which acts as a buffer to maintain the pH of the solution. In the case of a tin bath the tin salt would be furnished by Na_2SnO_3, the conducting salt by NaOH which also assists anode corrosion, the addition agent to effect the deposit being glucose or other organic materials.

From the industrial viewpoint the plating baths may be divided into a number of types, examples of which are the sulfate baths, the cyanide, the chloride, the perchlorate, the phosphate, and the solutions from which precious metals are deposited. In most cases a metal anode is the source of the plating metal. These are either as pure as can be commercially obtained or else specifically modified in their composition to affect the cathode deposit in a desirable manner. In a number of cases, however, the electrolyte constituents are the source and reservoir of ions for the cathodic deposit. Insoluble anodes are employed. In still other cases a combination of insoluble and active anode may be used as in the cadmium cyanide baths where both cadmium, which dissolves and forms Cd^{++} ions, and steel, which does not, are employed as anodes. Such a setup is made to balance anodic solution and cathodic deposition which occur at different rates.

Structure of Deposits. Electrodeposited metals all show crystalline structure upon X-ray examination. It appears that differences in their physical properties and appearances are caused by differences in the size and shape of the crystals. A number

of factors affect the characteristics of plated deposits,[2] such as current density, concentration and agitation of the solution, temperature, conductivity of the solution, metal ion concentration, H^+ ion concentration, the use of addition agents, the structure of the base metal, and the throwing power of the solution. This latter term refers to the characteristic of a plating bath in reference to its relative metal distribution on irregularly shaped objects. When this distribution is uniform, the bath is said to have good throwing power. Most conducting salts and substances that increase cathode polarization tend to improve throwing power.

Plating baths are operated within definite c.d. ranges, beyond which poor types of deposits result. Plating baths having low ionic metal concentration are in general use for the production of fine-grained or so-called "amorphous" deposits which are readily polishable. Such low ionic concentration is produced not by dilute solutions but either by the use of salts showing low ionization or salts whose ionization is depressed by the addition of another salt having a common ion, or by the employment of compounds producing the metallic ion not by primary but by secondary ionization, or by reduction by cathode products. Examples are the use of double salts such as $NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, complex compounds such as the double cyanides, and in the specific case of chromium, chromic acid. In general deposition potentials are lower than the decomposition voltage of water, but in the case of chromium or of alloys such as brass, the deposition potential is above that of the decomposition of water, and hydrogen is evolved at the cathode. The latter condition is essential for the deposition of chromium, and about 70 per cent of the current is consumed in hydrogen evolution. Plating bath current efficiencies are usually above 90 per cent. A large number of common and precious metals are commercially plated. The general characteristics of the baths employed are given in Table 28. After plating and drying, the objects may be polished, usually with mild abrasives such as tripoli and rouge on high-speed wheels.

Plating Equipment. Mechanical equipment for plating assumes many different forms. Small objects are usually plated

[2] BLUM, W., and HOGABOOM, G. B., "Principles of Electroplating and Electroforming," McGraw-Hill Book Company, Inc., New York, 1949.

in large quantities in barrels which rotate in the plating solutions. Larger objects are generally wired or hung on rods which in turn connect with cathode bars.   There has been an extensive development of automatic plating, in which the successive operations involved in the entire production flow sheet are mechanized by having the object hung on rods suspended from conveyors with automatic mechanisms causing the object to pass through differ-
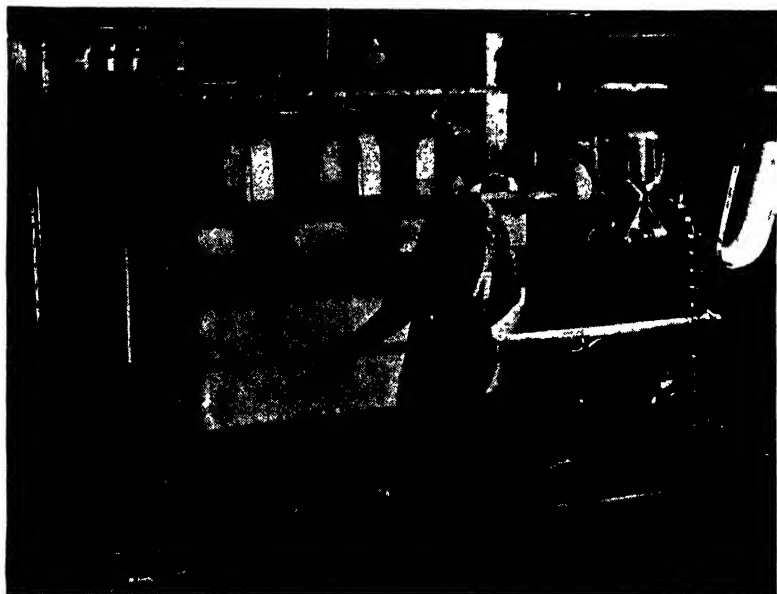
Fɪɢ. 59.   Automatic unit plating radiator shells, showing unload end.   (*General Motors Corporation.*)

ent baths such as cleaners, dips, plating solution, rising out of the tank at one end and dipping into the next one by a tripping and raising action connected to the conveyor.   Figure 59 shows a view of a machine of the type employed in the automotive industries for radiator plating, where the radiators receive successive finishes of copper, nickel, and chromium.

PLATING SOLUTIONS

In recent years a very extensive literature on electroplating has developed, particularly since the introduction of chromium plating and its wide application.   For greater detail than is given here, the reader is referred to some of the standard text-

TABLE 28. COMMON ELECTROPLATING BATHS

Metal	Bath type	Anode	Cathode c.d., amp/sq ft	Temperature, °C	Av. current efficiency
Brass...	Cyanide	Cu-Zn alloy	2–3	32–45	80
Cadmium.	Alkaline cyanide	Cd	10–50	20–30	
Chromium....	Chromic acid + sulfate	Pb	100–300	40–50	12–20
Cobalt...	Sulfate	Co	30–165	20–30	95–98
Copper......	Acid sulfate	Cu	15–40	25–50	97–100
	Alkaline cyanide	Cu	3–14	35–40	30–60
	Rochelle-cyanide	Cu	......	......	40–70
Gold...... ..	Cyanide	Au	1–5	60–80	70–90
Indium..........	Cyanide	In-Pt	....	......	30–50
Iron......... .	Chloride	Fe	100–180	90–110	90–98
	Double sulfate	Fe	20–30	20–30	95–98
Lead........ .	Fluoborate	Pb	5–20	20–30	98–100
	Perchlorate	Pb	20–30	20–30	95+
Nickel	Single sulfate	Ni	5–20	20–30	94–98
	Double sulfate	Ni	3–6	20–30	94–98
	Sulfate-chloride	Ni	14–50	50–60	94–98
Palladium... . ..	Chloride	Pd	10	.... ..	98–100
Platinum.... ...	Phosphate	Pt	1	70	
Rhodium...	Sulfate or phosphate	.....	20–80	40–50	10–20
Silver... . .	Cyanide	Ag	3–8	15–25	98–100
Tin.... . . .	Alkaline stannite	Sn	10	50	
	Alkaline stannate	Sn	5–15	60	70–95
	Acid sulfate	.....	.. ....	20–30	90–95
Zinc....	Sulfate	Zn	12–30	20–30	99
	Sulfate (hot)	Zn	80–100	50–60	
	Chloride	Zn	40–100	20–40	
	Alkaline cyanide	Zn	8–20	40–50	85–90

books on the subject.[3] The individual metals will be discussed in alphabetical order.

Aluminum. Aluminum cannot be deposited from aqueous solutions, but Keyes and Swann[4] electrolyzed Grignard com-

---

[3] *Ibid.;* FREEMAN, B., and HOPPE, F. G., "Electroplating with Chromium, Copper, and Nickel," Prentice-Hall, Inc., New York, 1930; LANGBEIN, G., "Electrodeposition of Metals," H. C. Baird & Co., Inc., New York, 1920; "Modern Electroplating," The Electrochemical Society, New York, 1942.

[4] KEYES, D. B., and SWANN, S., *Ind. Eng. Chem.*, **20**, 1068 (1928).

pounds, such as diethyl aluminum iodide and ethyl aluminum diiodide, in ether with an aluminum anode and a copper cathode to give smooth deposits of aluminum. The reaction chamber was cooled by means of an ice bath, the electrodes were 1 cm apart, the voltage was 40, and the current density was 0.02 amp per cm². Blue and Mathers[5] stated that aluminum could be deposited with a cathode efficiency above 75 per cent from a bath containing 20 g of $AlBr_3$, 20 g of $AlCl_3$, and 4 g of Al, in a solvent consisting of 40 cc of C_2H_5Br, 80 cc of C_6H_6, and 40 cc of $(CH_3)_2C_6H_4$.

Antimony. Antimony may be plated from the bath proposed by Roseleur consisting of 50 g of Sb_2S_3 dissolved in 100 g of Na_2CO_3 per liter, or in a chloride bath[6] containing 100 g of tartar emetic dissolved in 100 cc of water to which 200 cc of concentrated HCl is added.

Bismuth. Kern and Jones[7] investigated addition agents in bismuth electrolytes, and Harbaugh and Mathers[8] proposed a perchlorate bath consisting of 40 g of bismuth oxide and 104 g of $HClO_4$ per liter, with glue and cresol as addition agents. Fink and Gray[9] deposited lead-bismuth alloys from perchlorate baths.

Cadmium. The application of cadmium plating for rust-proofing has found extensive employment in metal manufacturing and the automobile industries. Cadmium may be plated from slightly acid chloride or sulfate solutions,[10] but the deposits are coarsely crystalline and not usually satisfactory unless some addition agents be present. In commercial plating the cyanide bath is ordinarily preferred.[11] The baths are prepared by the solution of $Cd(CN)_2$ or CdO in NaCN to which relatively large amounts of addition agents are added to produce brighter

[5] Blue, R. D., and Mathers, F. C., *Trans. Electrochem. Soc.*, **69**, 519, 529 (1936).

[6] Ghosh, J. C., and Kappanna, A. N., *J. Phys. Chem.*, **28**, 149 (1924).

[7] Kern, E. F., and Jones, T. R., *Trans. Am. Electrochem. Soc.*, **57**, 255 (1930).

[8] Harbaugh, M., and Mathers, F. C., *Trans. Electrochem. Soc.*, **64**, 293 (1933).

[9] Fink, C. G., and Gray, O. H., *Trans. Electrochem. Soc.*, **62**, 123 (1932).

[10] Mathers, F. C., and Marble, H. M., *Trans. Am. Electrochem. Soc.*, **25**, 297 (1914). For review on Cd plating, see "Modern Electroplating," pp. 101–114, The Electrochemical Society, 1942.

[11] Westbrook, L. R., *Trans. Am. Electrochem. Soc.*, **55**, 333 (1929).

deposits. Among these are glue, casein, molasses, goulac, the latter two being more common. Small amounts of cadmium solutions, either as the sulfate or as the chloride, are added to nickel baths as brighteners to increase the whiteness and brilliancy of the deposit. It is stated that small amounts of nickel are beneficial in cadmium baths. Anodes are of pure metallic cadmium, although both cadmium and steel are employed, the relative areas of which are adjusted according to operation conditions. Table 29 gives operating data. Nickel salts in small amounts may be added as brighteners.[12] Organic addition agents are often used.

Chromium. The commercial application of chromium plating is due to Fink,[13] who converted laboratory experiments into commercial practice. An extensive literature has been built up on the subject.[14] The metal is deposited at low current efficiencies, lead anodes being employed in a bath consisting of CrO_3 plus small amounts of sulfates. A typical simple bath is given as CrO_3 250 g per liter, H_2SO_4 1.25 to 2.5 g per liter, at current density of 100 to 300 amp per sq ft (10.8 to 32 amp per dm^2) and temperatures of 40 to 50°C. Many modifications of the bath exist, in that other sulfates such as those of chromium, sodium, potassium, and magnesium may be substituted for all or part of the H_2SO_4. It is stated that the most important constituents of the bath are CrO_3 and sulfate ion. The ratio between them should not be less than 100:1 and for the best throwing power should be about 200:1.[15] During deposition it is necessary to maintain a relatively thick film of hydrogen evolved at the piece being plated. In ordinary practice the cathode current efficiency is considerably below 20 per cent under the optimum plating conditions.

Chromium shows unusual resistance to oxidation and tarnish. The platings are very smooth and may be produced in mirrorlike finishes. These will resist color changes due to oxidation upon heating in air up to 480°C (900°F). When properly applied

[12] U.S. Patent 1,681,509.

[13] FINK, C. G., U.S. Patent 1,581,188 (Apr. 20, 1926).

[14] Patents: *Univ. Mich. Eng. Research Bull.* 8 (1927); literature: *ibid.*, 10 (1928); commercial practice: *ibid., Eng. Research Circ.*, 3 (1930).

[15] BLUM and HOGABOOM, *op. cit.*, p. 307. For review of Cr plating see "Modern Electroplating," pp. 117–143, The Electrochemical Society, 1942.

over a buffed metal, chromium has a bluish cast somewhat like that of polished platinum. Owing to the process of deposition, chromium is porous and therefore, when used alone, is very poor protection against corrosion. Upon iron or steel, it will not prevent rusting; upon brass, if the zinc content be 10 per cent or more, it appears to accelerate weather corrosion. Many decorative platings are only 0.00002 in. (0.0005 mm) in thickness, while very cheap platings produced in a minimum time may be only 0.000002 in. (0.00005 mm) thick. The application of a heavier coating not only increases the cost of plating many fold, but defeats its purpose in that fine cracks and other imperfections develop in the coating. Resistance to corrosion is best obtained by plating with successive layers of copper, nickel, and chromium. With such coatings, chromium will so protect the underlying deposits that the resistance to corrosion as measured with a salt spray will be about three times that obtained without this thin layer (0.00002 in.) of chromium. For best results the combined thickness of the plate should not be less than 0.0006 in. (0.0015 mm). Nickel i used as the intermediate coating between copper plate and chromium not only because of its ability to take a higher luster than copper, but because it is not etched by the chromic acid bath. Should the relative costs of the two metals in the future warrant it, the thickness of the copper deposit may be increased at the expense of the nickel.

The smoothness and the extreme hardness of chromium make it suited to uses where resistance to wear is essential, such as in printing plates, wrist pins, steering knuckles, tube-drawing dies, and forming dies. For the lighter duty, as in printing plates, coatings up to 0.0005 in. in thickness, requiring $\frac{1}{2}$ to 1 hr in time, are sufficient, but for the heavier duties about 0.005 in. platings are necessary. For various engineering applications, "hard" chromium and "porous" chromium deposits have been developed.

Cobalt. Although laboratory investigations of cobalt plating appeared to show promise, in that very high current densities were possible and fine deposits were secured, very little commercial cobalt plating is done. Two typical formulae are given by Kalmus and his associates:[16] the double-salt bath of $CoSO_4 \cdot$

---

[16] KALMUS, H. T., HARPER, C. H., and SAVELL, W. L., Electroplating with Cobalt, *Can. Dept. Mines, Mines Branch, Ann. Report* **334** (1915); *Trans.*

$(NH_4)_2SO_4 \cdot 6H_2O$ 175 g per liter; or the sulfate-chloride bath containing $CoSO_4 \cdot 7H_2O$ 504 g per liter, NaCl 17 g per liter, H_3BO_3 45 g per liter. Cathode current densities of 30 to 165 amp per sq ft (3.2 to 17.8 amp per dm^2) are employed at temperatures of 20 to 30°C.

Copper. The two principal baths in commercial use are the acid sulfate and the alkaline cyanide solutions. The former, while simple and easily operated, cannot be applied for direct deposition of copper on surfaces of metals which would displace copper from solution, so that the cyanide copper bath finds extensive application in plating iron. Copper deposits often serve as a base for ornamental finishes and for subsequent plating with other metals. The acid copper bath consists of $CuSO_4$, usually as bluestone ($CuSO_4 \cdot 5H_2O$), and H_2SO_4. The concentration of the two constituents may vary within wide limits, the $CuSO_4 \cdot 5H_2O$ generally held between 150 and 240 g per liter. The cyanide copper bath is essentially a solution of sodium cuprocyanide, the formula of which is probably $2NaCN \cdot CuCN$ or $Na_2Cu(CN)_3$. Instead of being made directly from cyanides, the bath may be prepared from basic cupric carbonate and NaCN with Na_2CO_3. For the production of thick deposits of copper on metals such as iron, it is usual to put on an initial coating of copper from a cyanide bath, followed by deposition of the major part of the coating in an acid sulfate solution.

The copper cyanide-sodium potassium tartrate baths (KNa-$C_4H_4O_6 \cdot 4H_2O$, Rochelle salts) have found commercial use. The copper-plating, baths are tabulated in Tables 29 and 30. In general the sulfate baths are used for electrotyping, electroforming, and for immersion copper coating, whereas the cyanide electrolytes find application for ornamental finishes and undercoats for other metals.[17]

Gold. Gold is commonly plated from cyanide baths in which the gold is present as $KAu(CN)_2$, with rolled gold anodes. The solutions in use vary greatly in concentration, depending upon the thickness of the desired deposit and its color. Baths usually

---

Am. Electrochem. Soc., **27**, 75 (1915). For review of Co plating, see "Modern Electroplating," pp. 145–153, The Electrochemical Society, 1942.

[17] For reviews on acid copper, see "Modern Electroplating," pp. 155–171, The Electrochemical Society, 1942; for cyanide copper, *ibid.*, pp. 173–183; Rochelle salts copper, *ibid.*, pp. 185–198.

have a low content of free cyanide, the potassium salt being preferred. Small amounts of sodium phosphate increase the conductivity of the bath and may through complex formation lower the metal ion content.[18] A typical formula would show metal gold (as cyanide) 2.1 g per liter, KCN 15 g per liter, $Na_2HPO_4 \cdot 12H_2O$ 4 g per liter, while another bath contains metal gold (as cyanide) 4.2 g per liter, KCN 15 g per liter, operated at a cathode current density of 1 to 5 amp per sq ft (0.1 to 0.5 amp per dm²) at relatively high temperatures of 60 to 80°C. The higher current density is used for more concentrated solutions or at the higher temperatures. Under good operating conditions the cathode current efficiency is nearly 100 per cent. To avoid building up the gold content of the solution during use, carbon or platinum anodes may displace part of the gold anodes.

Gold deposits of 14 carat shades are produced from solutions to which copper salts are added; green gold by the addition of AgCN; red gold by the addition of CuCN or $Cu(C_2H_3O_2)_2$; white gold by the addition of double nickel cyanide to a gold bath. In all these cases there is a simultaneous deposition of two metals and a resultant alloy formation.

An interesting application is the commercial preparation of continuous films of gold 0.000002 in. thick, several inches wide, and hundreds of feet in length. Silver is rolled to foil thickness and continuously plated with gold. The duplex metal is treated in a nitric acid bath to dissolve the silver. The gold film is transferred to wax paper as a support. For book lettering and decorative purposes the product is competitive with mechanically beaten gold leaf.[19] In other processes, gold is deposited on stainless-steel or chromium-plated belts, sprayed with lacquer-type stripping materials, and removed from the cathode.

Indium. Westbrook[20] indicated that 200 g of In_2O_3 dissolved in a solution containing 120 cc of 96 per cent H_2SO_4 and 250 g of $Na_3C_6H_5O_7 \cdot 11H_2O$ per liter, with platinum anodes, at 18.6 amp per sq ft, gives a satisfactory indium deposit. Gray[21]

[18] For review on gold plating, see "Modern Electroplating," pp. 199–210, The Electrochemical Society, 1942.

[19] U.S. Patent 1,731,415, Wm. F. Grupe to Peerless Roll Leaf Co., Inc. (Oct. 15, 1929).

[20] WESTBROOK, L. R., *Trans. Am. Electrochem. Soc.*, **57**, 289 (1930).

[21] GRAY, D., *Trans. Electrochem. Soc.*, **65**, 381 (1934).

studied the effect of addition agents and showed that, when indium is deposited with gold and a little silver and heat-treated at 1500°F, a sky-blue colored gold is produced. Murray[22] proposed a bath of 37.5 g of indium potassium cyanide, 67.5 g of free KCN, and 18 g of sucrose per liter.

Iron. Iron is often plated as a thin coating on the surface of printing blocks or engraving dies; but it has been displaced to a considerable extent for this purpose by nickel or chromium. It is still used for producing a relatively hard surface on copper etching plates. An important industrial application of iron deposition is the building up of worn or undersized parts of machinery, where relatively thick deposits are required. This was developed in England to meet a war need and was reported in 1920 by MacFadyen.[23] A cold concentrated solution of ferrous ammonium sulfate was used at low current density. MacFadyen also showed that much higher current densities could be used if the bath were run warm. This work was later taken up by the Westinghouse Electric & Manufacturing Company[24] where a bath of this type was worked at current densities of 6.5 to 11 amp per dm^2 (60 to 100 amp per sq ft) by raising the bath temperature to 50 and 70°C (122 and 158°F). Typical chloride baths are given in Table 31 and sulfate baths in Table 30. The baths have the disadvantage that there is a tendency of the ferrous salts to oxidize to ferric, especially when the solutions are nearly neutral, so that frequent regulation is required.

Lead. Lead is plated to a small extent for certain military purposes and in connection with chemical apparatus and other minor uses. Suitable dense deposits can be produced only from the fluosilicate, fluoborate, and perchlorate baths.[25] The first is a modification of the electrolyte used in the Betts lead-refining process. A typical fluoborate bath is given as $Pb(OH)_2 \cdot PbCO_3$ dissolved in a fluoboric acid made from 50 per cent HF and H_3BO_3, with glue as addition agent. Operating details are given in Table 31. Mathers[26] recommends a perchlorate bath con-

[22] Murray, W. S., *Ind. Eng. Chem., News Ed.*, **11**, 300 (1933).

[23] MacFadyen, W. A., *Trans. Faraday Soc.*, **15**, 98 (1920).

[24] Kellogg, D. R., *Mining and Met.*, **3**, 61 (1922).

[25] For review of lead plating baths, see "Modern Electroplating," pp. 221–233, The Electrochemical Society, 1942.

[26] Mathers, F. C., *Trans. Am. Electrochem. Soc.*, **23**, 159 (1913).

taining 5 to 6 per cent lead, 2 to 5 per cent $HClO_4$, and 0.05 per cent of peptone or clove oil, operated at a current density of 20 to 30 amp per sq ft (2 to 3.2 amp per dm^2) at 20 to 30°C. It appears necessary to have heavier deposits of lead than are usual for nickel, zinc, and other metals, before impervious coatings are secured.

Nickel. A large number of formulae have been developed for nickel plating. All of them were of the same general type, *i.e.*, nearly neutral or slightly acid solutions in which the nickel is present principally as a simple salt, usually the sulfate. A number of variations exist in the bath formulae when platings are to be made on zinc, zinc base. and aluminum base die castings, and nonferrous metals.[27] Typical single- and double-salt baths are given in Table 30. In commercial work considerable emphasis is placed on the proper acidity in the bath and the maintenance of this acidity.

Deposits of nickel thicker than the usual 0.0002-in. plate are costly when the standard pH of 5.3 and above is employed. It has been shown [8] that nickel baths may be operated with pH's below 3, at which point much higher current densities are possible and good heavy deposits obtained. In the low pH bath the nickel content is kept constant by a uniform anode dissolution. No peeling or cracking at the edges is apparent. The bath remains clear. With the low pH bath, however, there is a greater tendency toward pitting. Cathode efficiencies are approximately 75 per cent as compared with 95 per cent with the standard pH. Lower bath temperatures are recommended for the low pH bath. Zinc base die castings are more difficult to plate with the low pH solutions. In the operation of the ordinary high pH bath, platers worry about satisfactory anode corrosion. With low pH there is rapid corrosion of the anodes with a tendency to accumulate too much nickel in solution. This factor, however, is converted into an advantage by replacement of a portion of the nickel anodes by lead anodes which decrease the tendency for pitting of the cathode deposits. Low pH baths do not necessitate as careful control as those of high pH.

The operation of nickel solutions is complicated by the behavior

---

[27] For review of nickel plating, see "Modern Electroplating," pp. 235-274, The Electrochemical Society, 1942.   ●

[28] PHILLIPS, W. M., *Trans. Am. Electrochem. Soc.*, **58**, 387 (1930).

of the anodes, in that pure nickel shows a tendency toward passivity. To overcome passivity and to aid in the solution of the anode, appreciable amounts of carbon and iron were formerly added during the casting of the anodes, so that anodes containing only 88 to 92 per cent nickel and 3 to 8 per cent iron were most frequently used. It has been shown that small amounts of sulfur in high-purity anodes depolarize them and eliminate passivity, so that the anodes now used contain at least 99 per cent nickel (plus cobalt) and not more than 0.35 iron, 0.10 copper, and 0.05 sulfur. To avoid the difficulties of irregular corrosion of the anodes, they are given a preliminary electrolysis as anode in a 5 per cent HCl solution by the manufacturers. After this treatment the anode corrosion is generally uniform. It is aided by the addition of chlorides to plating baths.

For the electrodeposition of "bright" nickel having a grain size of less than 0.0001 mm, Schlotter[29] proposed an electrolyte having a pH between 2.5 and 4.5 and containing a polysulfonate such as nickel benzene disulfonate or the naphthalene trisulfonate with nickel sulfate or chloride and boric acid. Stocker[30] reviewed bright nickel plating. Exacting attention must be paid to freedom from contamination and metals other than nickel.

Lustrous deposits of nickel-cobalt alloys, according to Weisberg,[31] are obtained from a bath containing 240 g $NiSO_4$, 45 g $NiCl_2$, 35 g $NaCHO_2$, 30 g boric acid, 15 g cobalt sulfate, 2.5 g $(NH_4)_2SO_4$, 1 g formaldehyde, at a pH of 3.7, current density of 40 amp per sq ft, and a temperature of 60°C.

Wesley[32] showed that thick electrodeposits of nickel have a wide field of application in salvaging worn or mismachined parts and in the manufacture of bimetals.

Palladium.[33] Palladium may be plated from the same type of baths as given for platinum by the substitution of a palladium salt for the corresponding platinum salt. Good deposits are obtained only at 1.2 to 1.5 volts, which is below the gas evolution point.

[29] SCHLOTTER, M., U.S. Patent 1,972,693 (1934).

[30] STOCKER, O. A., *Monthly Rev. Am. Electroplaters Soc.*, February, 1939.

[31] WEISBERG, L., *Trans. Electrochem. Soc.*, **73**, 435 (1938).

[32] WESLEY, W. A., *Monthly Rev. Am. Electroplaters Soc.*, **25**, 581 (1938).

[33] For review, see SCHUMPEL, K., The Electrodeposition of the Metals of the Platinum Group, pp. 275–284 of "Modern Electroplating," The Electrochemical Society, 1942.

Platinum. Small amounts of platinum are plated from a phosphate or a diamino nitrite bath[34] following typical formulae given in Table 32, with platinum or carbon anodes, both of which are insoluble. Difficulty is encountered in securing thick impervious deposits, whereas thin ones are not protective against corrosive attack, owing to the fact that they show fine cracks, probably caused by the contraction of the platinum during deposition. The rate of deposition is low in the phosphate bath, being of the order of 8 mg per amp-min. The metal contents of the bath are maintained by the addition of platinum salts.

Rhenium. Fink and Deren[35] state that rhenium may be plated from perrhenates or perrhenic acid with H_2SO_4 to give bright, hard deposits of the metal which is quite resistant to H_2SO_4.

Rhodium. Rhodium chloride or sulfate electrolytes do not yield satisfactory plating solutions. Electrolytes are made up from acid phosphate rhodium salts in concentrated form. Two electrolytes find commercial application, each containing 2 g of metallic rhodium: in the first, 35 g H_2SO_4 per liter; and in the second, 10 to 40 cc 85 per cent H_3PO_4 per liter. Insoluble anodes of platinum are used, the rhodium solution being added to replace metal which is deposited. The average platings are only light flashes which are very thin, having thicknesses of the order of 0.000005 (1 mg rhodium per sq in.), and are generally deposited on a nickel undercoat.

The nontarnishing characteristics of rhodium make it valuable in reflectors. Mirror reflectors[36] for searchlights 158 cm (62 in.) in diameter are electroformed on a previously electroformed mold having a nickel surface. The mold is held in a metal frame, and the back is stopped off with lacquer. A deposit of 0.0015 cm (0.0006 in.) nickel is first made, followed by 0.003 cm (0.0012 in.) of copper. The whole is then placed in a bronze ring and heavily copper plated, 0.6 cm (0.25 in.). After the deposit is stripped away, the nickel surface is given a flash plating of rhodium.

Silver. Silver plating is always done from cyanide solutions, in that deposition from simple salts results in very coarse crystal-

---

[34] KEITEL, W., and ZSCHIEGNER, H. E., U.S. Patents 1,779,436 and 1,779,-457.

[35] FINK, C. G., and DEREN, P., *Trans. Electrochem. Soc.*, **66**, 471 (1934).

[36] KUSHNER, J. B., *Metals & Alloys*, **11**, 137 (May, 1940).

line deposits and the metallic surfaces which are being plated would tend to precipitate the silver from its simple salts.[37]   The solution is a double cyanide, either $KAg(CN)_2$ or $NaAg(CN)_2$, the former being preferred in that potassium compounds show greater conductivity and that carbonates formed in the solution are more soluble than the corresponding sodium salts.   A typical formula for white deposits is AgCN 35 g per liter, KCN 37 g per liter, K_2CO_3 38 g per liter; and for bright deposits AgCN 36 g per liter, KCN 52 g per liter, K_2CO_3 38 g per liter, to which very small amounts of CS_2 are added as a brightener.   Anodes are rolled silver 999 fine.   When the bath contains sufficient free cyanide, these dissolve readily with very little anode polarization. Cathode current densities are low, being 3 to 8 amp per sq ft (0.3 to 0.8 amp per dm²) at 15 to 25°C, voltages of 1 to 2 usually being sufficient.   Cathode current efficiency in silver deposition is usually very close to 100 per cent.

Tin.   Tin plating[38] finds application as a covering for copper and steel in cooking kettles for food products, refrigerator coils in machines of the electric type, and a number of cases where decorative coverings are desired.   A typical alkaline stannite bath is $SnCl_2 \cdot 2H_2O$ 30 g per liter, dissolved in NaOH 75 g per liter with glucose 60 g per liter as addition agent.   The bath is operated at a cathode current density of about 10 amp per sq ft (1 amp per dm²) at 50°C.   The stannous chloride first reacts with the NaOH with the formation of $Sn(OH)_2$, which in turn reacts with more NaOH to form Na_2SnO_2.   A typical stannate bath is Na_2SnO_3 180 g per liter, $SnCl_2 \cdot 2H_2O$ 2 g per liter, with 0.2 g per liter of rosin dissolved in NaOH as addition agent.   A modified bath[39] is given in Table 31, based on sodium stannate and an oxidizing agent such as H_2O_2 or sodium perborate to maintain the tin in the stannic form and sodium acetate as a buffer.   Pure tin anodes are used.

[37] For review of silver plating, see "Modern Electroplating," pp. 285–313, The Electrochemical Society, 1942.

[38] See chapters on Tin Plating, Hot Dipped Coatings, Electrolytic Tin Plate, in Mantell "Tin, Its Mining, Production, Technology, and Applications," 2d ed., Reinhold Publishing Corporation, New York, 1949.   For review of acid sulfate electrolytes see pp. 315–327 and for alkaline baths pp. 329–341 of "Modern Electroplating," The Electrochemical Society, 1942.

[39] U.S. Patents 1,841,978 and 1,919,000.

Tin Plate, Electrolytic. With the development of high-speed rolling of continuous strip by the steel industry, plus wartime emphasis on conservation of tin, there was a decided impetus to the development of electrolytic tin plating. The factors involved concern themselves with the electroplating baths, their stability, and, for the purpose of speed, their operation at high current densities, and second, with the mechanical and electrical factors in the handling of long lengths of strip steel at high speeds continuously.

Electrolytic tin-plating lines[40] might be divided into types in which the sodium stannate bath is employed as the electrolyte in one case, and acid baths in the other; into those in which the sheet is handled and caused to pass vertically and over rolls for change of direction with vertical anodes and another type in which the sheet is processed horizontally, commonly with horizontal anodes. These differences result in markedly different mechanical and electrical arrangements.

The alkaline baths consist essentially of either sodium stannate and caustic soda or potassium stannate and potassium hydroxide electrolytes. Agents to oxidize traces of stannites may be added, as well as buffer salts such as acetates. The current density of the sodium stannate baths is approximately 20 to 30 amp per sq ft; the temperature is 180 to 190°F (82.2 to 87.8°C). Current efficiencies are from 60 to 80 per cent.

The acid bath is primarily composed of stannous sulfate and an aromatic sulfonic acid, with addition agents. The use of colloidal addition agents is essential for successful operation.

Possible current densities with various types of baths vary from 10 to 400 amp per sq ft. Bath temperatures range from 70 to 100°F (21.1 to 37.8°C). Cathode and anode current efficiencies are nearly 100 per cent.

Halogen electrotin-plating solutions contain tin chlorides and fluorides with an organic addition agent. The tin content may be varied from 15 to 40 g per liter, depending on current density and the speed of the strip, the organic addition agent being about 2 g per liter. The bath is operated at a pH of 2.7 with an optimum temperature of 150°F (65.6°C). A range of current densities from 50 to 500 amp per sq ft is possible with various

[40] MUNGER, H. P., *Iron Steel Engr.*, **21**, 53 (March, 1944); LIPPERT, T. W., *Iron Age*, **194**, 29 (March, 1942).

compositions of the solution, but is ordinarily in actual operation 185 amp per sq ft. Cathode and anode current efficiencies are said to be 97 and 100 per cent, respectively.

Electroplated tin on steel strip does not have the smooth reflecting surface of hot-dipped tin. For many applications, the electroplated surface perhaps with scratch brushing or little polishing is sufficient. For general application, "reflow" or melting units which fuse the electroplated coating have become a portion of the tinning line.

As a general statement, although there may be exceptions, it is easier and more economical to put on heavier coatings (from 1 lb and upwards of tin per base box of tin plate) by hot dipping and lighter coatings (from $\frac{3}{4}$ lb of tin and lower per base box of tin plate) by electrolytic processes.

The physical space of the electroplating part of the line is small in comparison to the electrical, mechanical, physical control and inspection portions, so that the engineering development of equipment plays an important part. If the electrolyte were changed to that of another metal, other plated steels might be made.

In an electrolytic tin line there are three factors to be considered: (1) the handling of the strip, (2) the proper cleaning of the strip surface, and (3) the plating of the strip. A fourth factor, that of fusion of the tin plating, is important in most lines. Plating line speeds vary from about 500 to 1,000 fpm. The higher speed lines have been operated as rapidly as 1,350 fpm.

Tungsten. Fink and Jones[41] plated tungsten from a bath containing 60 g NaOH, 38 g sodium tungstate, and 60 g dextrose per liter. Yntema[42] deposited tungsten from a citric acid bath, and Holt and Kahlenberg[43] from an alkaline phosphate solution. Holt maintained[44] that iron is present with tungsten in the cathode deposit.

Zinc. For protection against rust, large tonnages of steel are coated with zinc by galvanizing, in which the cleaned article is coated by immersion in a bath of molten zinc. In other cases,

[41] FINK, C. G., and JONES, F. L., *Trans. Electrochem. Soc.*, **59**, 461 (1931).

[42] YNTEMA, L. F., *J. Am. Chem. Soc.*, **54**, 3775 (1932).

[43] HOLT, M. L., and KAHLENBERG, L., *Metal Ind.* (New York), **31**, 94 (1933).

[44] HOLT, M. L., *Trans. Electrochem. Soc.*, **66**, 453 (1934).

as in sherardizing, the object is heated with zinc dust which sinters on the surface. In electrogalvanizing, the zinc coating is plated. Zinc can be deposited from its sulfate, chloride, acetate, double cyanide, and alkaline zincates, all of which are soluble. The principal baths are the acid sulfate and the alkaline cyanide solutions.[45] The latter show better throwing power and are

TABLE 29. CYANIDE BATHS
(Grams per liter)

	Cu	Rochelle Cu	Brass	Bronze	Zn	Bright Zn	Cd
CuCN..................	22.5	26	27	30			
Zn(CN)₂.	. .	....	9	2.3	60	60	
NaCN total............	34	35	54	37	23	42	90
NaCN free....	9	5.5	7	0.4	....	.....	7.5–30
CdO	.	.....	....	....	....	. ...	30
Na₂S₂O₃..	0.2						
NaOH...............	. ...				53	79	
Rochelle Salts..... ...		30	. ...	15			
Na₂CO₃	15	30	30				
Addition agent	. . .	....	.... .	....	. ...	.....	X
Temperature, °C. . .	25–40	60–70	25–40	25–40	40–50	24–30	25–40
pH	....	12 6					
C.d., amp. per sq. ft .	3–15	20–60	3–5	2–4	8–20	5–50	10–50
Voltage.................	1.5–2	2–3	2–3	2–3			
Anodes	Cu	Cu	80 Cu, 20 Zn	92 Cu, 8 Zn	Zn	Zn	Cd and steel
Anode area..............	......	2x cathode					
Anode efficiency, per cent..	... .	50–70					
Cathode efficiency, per cent	.. . .	40–70	....	....	....	.....	75–90

most useful for parts with deep recesses. Purity of the coating is an important consideration in that even small amounts of foreign metals reduce its protective value. Sulfate solutions show less tendency for metallic impurities from the anodes to be deposited at the cathode than do cyanides. Emphasis should thus be placed on the advantage of pure anodes. A typical sulfate formula is given in Table 30 with which licorice is used as an addition agent for the production of brighter deposits; a typical chloride bath is given in Table 31 and a cyanide bath in

[45] For review of zinc plating, see "Modern Electroplating," The Electrochemical Society, 1942, pp. 343–358 for acid zinc, pp. 359–380 for cyanide

Table 29.   Electrolytic zinc or zinc-mercury[46] or zinc-aluminum-mercury[47] anodes are used. . These special anodes show improved anode corrosion and decreased solution attack, particularly at the water line.   Pure zinc electrodes are needed for "bright" zinc plating.   In general, the cyanide solutions produce either dull or bright deposits with good throwing power, and the acid solutions give smooth white deposits having poor throwing power.

Alloy Plating.   Under certain conditions it is possible to deposit two metals simultaneously from a solution containing both, under which conditions the deposition potentials of the metals are fairly close.   An alloy commercially deposited on an industrially important scale is brass, a typical bath for which is CuCN 27 g per liter, $Zn(CN)_2$ 9 g per liter, NaCN 54 g per liter, Na_2CO_3 30 g per liter, operated with brass anodes of 67 to 80 per cent copper at cathode current density of 2 to 3 amp per sq ft (0.2 to 0.3 amp per dm^2) at 32 to 45°C.   Copper-tin alloys or bronzes find commercial application, in most cases so-called "bronze platings" being produced in brass-plating solutions of high copper content.

Bronze anodes[48] containing 90 per cent Cu plus 10 per cent Sn were found to dissolve unsatisfactorily in oxalate baths and to give a slime rich in tin.   In cyanide baths the bronze anodes dissolved cleanly and brightly, so that easy control of Cu-Sn concentration has been maintained in cyanide-stannate baths by bronze anodes during long periods of deposition.[49]

The normal deposition potentials for copper and zinc are far apart, being $+0.34$ and -0.076, respectively, in sulfate electrolytes.   Brass plating is rendered possible by the fact that in forming double cyanides the potential of copper is reduced more rapidly than that of zinc, and finally the two become equal.   The potential of copper may be made lower than that of zinc by a still further addition of cyanide, so that a solution can be produced in which copper will precipitate zinc by immersion.

[46] U.S. Patents 1,435,875; 1,451,543; and 1,497,265.

[47] GRAHAM, A. K., *Trans. Electrochem. Soc.*, **67**, 269 (1935); U.S. Patents 1,887,841; 1,888,202; and 2,064,307.

[48] BAIER, S., and MACNAUGHTAN, D. J., *Metal Ind. (London)*, **47**, 543 (1936); *J. Electrodepositors' Tech. Soc.*, 11 (1936); MATHERS, F. C., and SOWDER, S., *Trans. Electrochem. Soc.*, **37**, 525 (1920).

[49] BAIER, S., and MACNAUGHTAN, D. J., *Metal Ind. (London)*, **47,** 543 (1936); *J. Electrodepositors' Tech. Soc.*, **11,** (1936).

TABLE 30. SULFATE BATHS
(Grams per liter)

	Cu	Zn	Single Ni	Double Ni	Low pH Ni	Black Ni	Fe	Co
CuSO₄·7H₂O	200							
ZnSO₄·7H₂O		240				38		
NiSO₄·7H₂O			105		230	75		
NiSO₄(NH₄)₂SO₄·6H₂O				75		45		
FeSO₄(NH₄)₂SO₄·6H₂O							350	
CoSO₄(NH₄)₂SO₄·6H₂O								175
Al₂SO₄·18H₂O		30						
H₂SO₄	50						0.2	
H₃BO₃			15	15	30			
NiCl₂·6H₂O			15		68			
NH₄Cl		15	15	1		15		
NaCNS								
Temperature, °C.	25–50	25–50	25–30	20–30	60–70	20–25	20–30	20–30
pH		3.5–4.6	5.3–5.8	5.3	1.5	6.6		
C.d., amperes per square foot	15–40	5–50	5–20	3–6	30–50		20–30	30–165
Voltage	0.75–2.0		1.5–2		3–4	0.75–1.0		
Anodes	Cu	Zn or Zn-Hg	Ni	Ni	Ni			
Anode area	> Cathode		> Cathode	> Cathode	> Cathode			
Remarks			Anode bags			¼ Ni, ¾ C		

In cyanide baths, individual copper and zinc anodes were first attacked in proportion to their exposed areas. By suitable choice of area ratio (actually, anode current density) the proportion of zinc and copper can be easily controlled during long periods of electrolysis.

TABLE 31. CHLORIDE AND OTHER BATHS
(Grams per liter)

	Fe	Au	Cr	Sn	Zn	Pb
$FeCl_2 \cdot 4H_2O$	300					
$CaCl_2$	150					
HCl, free	55	82				
$AuCl_3$	......	50				
$ZnCl_2$	......	......	....	....	136	
NaCl	......	......	....	....	234	
$AlCl_3 \cdot 6H_2O$	......	.....	......	....	20	
CrO_3	......	......	250			
H_2SO_4	......	......	1–2			
Na_2SnO_3	......	......	....	120		
NaOH	......	......	....	10		
$NaC_2H_3O_2$	......	......	....	15		
H_2O_2 (100 volumes)	......	......	....	0.5		
$Pb(OH)_2PbCO_3$	......	......	....	....	......	150
HF (50 per cent)	......	......	....	.. .	......	240
H_3BO_3	......	......	....	....	... ..	105
Addition agent	......	......	....	....	.....	X
Temperature, deg. C.	90–110	25	40–50	....	20–30	20–30
pH	1 8					
C.d., amp./sq. ft.	60–100	5	100–300	6–60	40–100	5–20
Voltage	......	2–3	....	4–6		
Anodes	Pure Fe	24K Au	Pb	Sn	Zn	Pb
Anode c.d.	......	.....	....	5–25		
Remarks	Anode bags					

Lead and tin have nearly equal potentials in fluoborate solutions, and lead-tin alloys are deposited from such baths with cathode current efficiencies over a wide range of conditions of nearly 100 per cent.

Faust[50] reviewed the bibliography of alloy plating. Many thousand pounds of useful alloys are electrodeposited in decorative and protective finishing of metals and in engineering appli-

[50] FAUST, C. L., *Trans. Electrochem. Soc.*, **78**, 383 (1940).

cation. In certain composition ranges, alloy deposits have been found more corrosion resistant, more protective for the basis metal, brighter than either metal alone, more readily buffed, tougher and more adherent to the basis metal, more suitable for subsequent plates, and deposited satisfactorily over a wider range

TABLE 32. PRECIOUS METALS
(Grams per liter)

	Ag	Au	Pt		Rh		Pd
AgCN, troy ounces per gal.	2 5-4 3						
H₂Pt₂Cl₆·6H₂O	..		4				
Pt salt[1]				10			
KAu(CN)₂, oz..		0 5-1 0					
KCN, free	4-7						
KCN, total .	5.2-9 1	0 5-1 5					
Pd salt[2]	... .				.....		10
H₃PO₄ (85 per cent)	....				10-40 cc		
K₂CO₃	5-15						
(NH₄)₂HPO₄.				20			
Na₂HPO₄.... .		2		100			
NH₄NO₃ ..				100			100
NaNO₂ ..				10			10
NH₄OH, cc				50			50
H₂SO₄ ..	..	.				35	
Rh (calc. as metal)	....	....	.....		2		
Temperature	72-78°F.	140-160°F.	70-90°C.	95°C.	110-120°F.	110-120°F.	
pH	....	. ..	7+	2-2 5			
C.d., amp./sq. ft .	5-15	.....	9.3	50-120	10-80	10-80	
Voltage .	1-2	2-4	3-4	4 5	2 5-5	2 5-5	1 2-1 5
Anodes	Ag	Au or C or stainless steel	Pt or C	Pt or C	Pt	Pt	

[1] Platinum diammino nitrite, 61 per cent Pt.
[2] Palladium diammino nitrite.

of operating conditions than can one or both of the individual metals. In several instances current efficiency has been improved and actual deposition of a metal such as tungsten, or deposition of nickel and iron from cyanide baths, has been made possible by codeposition with a second metal. Electrodeposition has successfully produced alloys where other methods have failed. Electrodeposited alloys usually have fine grain size, uniform structure, and are amenable to the customary metallurgical heat-treatments. The alloys are produced cold, hence need not be subjected to undesirable heating.

A variety of applications are possible. In decorative plating

Ni-Co,[51] Ni-Zn[52] (or Ni-Cd, etc.), Cu-Zn,[53] Cu-Sn,[54] Zn-Mo,[55] Ni-Mo,[56] and Au alloy deposition have been successfully established. In protective finishing, where corrosion conditions are so variable, no definite groups of alloy deposits have been established, but Cd-Zn,[57] Cu-Sn,[58] W-Ni,[59] Ni-Co,[60] Sn-Zn and Pb alloys with either Tl,[61] Bi,[62] Sn,[63] or Ag[64] look interesting.

Advantages have been found in electrodeposition of bearing metals, such as Ag-Pb,[64,65] Ag-Cd,[66] Pb-Sn,[67] Cu-graphite,[68] Sn-graphite,[69] and Cu-Pb[70] alloys. Certain advantages result from alloy deposition in bearing manufacture: (1) thin liners can be produced with relatively little aftermachining and scrap problem; (2) preparation in a "cold casting" process does not

[51] WEISBERG, L., *Trans. Electrochem. Soc.*, **73**, 435 (1938); **77**, 223 (1940); *Steel*, **99**, 43 (July 13, 1936).

[52] Proprietary Bright Nickel.

[53] Extensive use is well known.

[54] *Tin and Its Uses*, No. 5, p. 15 (April, 1940).

[55] Proprietary Bright Zinc.

[56] HOFFMAN, R. A., and HULL, R. O., *Am. Electroplaters' Soc.*, (June 1939).

[57] BLUM, W., STRAUSSER, P. W. C., and BRENNER, A., *J. Research Natl. Bur. Standards*, **16**, 185 (1936); STOUT, L. E., and FAUST, C. L., *Metal Ind.* (*N.Y.*), **28**, 381 (1930); FINK, C. G., and YOUNG, C. B. F., *Trans. Electrochem. Soc.*, **67**, 311 (1935); SCHWARZ, F., *Oberflächentech.*, **12**, 82 (1935).

[58] HEUSSNER, C. E., *Am. Soc. Testing Materials*, p. 14 (April, 1938); Intern. Tin Research Development Council, *Fourth Gen. Report, Pub.* 95 (1939).

[59] FINK, C. G., and JONES, F. L., *Trans. Electrochem. Soc.*, **59**, 461 (1931).

[60] WEISBERG, L., *Trans. Electrochem. Soc.*, **73**, 435 (1938); **77**, 223 (1940); *Steel*, **99**, 43 (July 13, 1936); FINK, C. G., and LAH, K. H., *Trans. Electrochem. Soc.*, **58**, 373 (1930); **72**, 458 (1937).

[61] FINK, C. G., and CONARD, C. K., JR., *Trans. Electrochem. Soc.*, **58**, 457 (1930).

[62] FINK, C. G. and GRAY, O. H., *Trans. Electrochem. Soc.*, **62**, 123 (1932).

[63] BLUM, W., and HARING, H. E., *Trans. Electrochem. Soc.*, **40**, 287 (1921).

[64] FAUST, C. L., and THOMAS, B., *Trans. Electrochem. Soc.*, **75**, 185 (1939); *Metal Ind.* (*London*), **55**, 253 (1939).

[65] DAYTON, R. W., and FAUST, C. L., Chap. 8, "Silver in Industry," edited by L. Addicks, Reinhold Publishing Corporation, New York, 1940.

[66] FAUST, C. L., *Trans. Electrochem. Soc.*, **78**, 383 (1940).

[67] BELYAEV, P. P., and BIRMAN, YA. N., *Novosti Tekhniki* 1936, No. 42–43, 21; *Vestnik Metalloprom.* (*U.S.S.R.*), **17** (9) 88 (1937).

[68] FINK, C. G., and PRINCE, J. D., *Trans. Electrochem. Soc.*, **54**, 315 (1928).

[69] Intern. Tin Research Development Council, *Pub.* 95 (1939).

[70] BELYAEV, P. P., VALEEVA, A. G., and HEL'MAN, S. P., *Chimie & industrie*, **35**, 855 (1935); *Vestnik Metalloprom.* (*U.S.S.R.*), **15**, 117 (1935).

subject the backing material to heat-treatment or tempering; (3) alloys can be made of metals difficult to alloy in any other way;[71] (4) unusually fine grain size and structural uniformity are obtained. Sensitive high-temperature thermopiles,[72] iron alloys having exceptional magnetic properties,[73] alloys for electroforming thin sheets,[74] and alloy materials that can be electrodeposited for building up worn parts or for special surfacing have been proposed. Cu-Zn alloy of exact composition has been deposited for many years as a bonding layer for rubber coating of steel.[75] Another application provides a Ag-Cu alloy for an undercoat for enamel.[76] Intermediate alloy layers are deposited to improve subsequent nickel and chromium or other plates.[77] Solder refining and manufacturing by electrodeposition have been done for many years.[78]

Single deposition studies might even show little possibility of alloy deposition with some metals in certain baths: for example, Ni and Fe from cyanide or W from alkaline baths, which, if tried in single deposition, would be discarded as unfavorable for alloy deposition. When these metals are in such "nonplating" baths containing other metals that can deposit out, the "unplateable" metal will codeposit under certain conditions. For example, Cu-Ni,[79] Cu-Fe,[80] Cu-Zn-Ni,[81] Cu-Ni-Fe,[82] Ag-Ni,[83] Au-Ni[84] have

[71] FAUST, C. L., "Modern Electroplating," pp. 67–75, The Electrochemical Society, 1942; DAYTON and FAUST, *op. cit.*

[72] KERSTEN, H., and SCHAFFERT, R., *Rev. Sci. Instruments*, **3**, 189–195 (1932).

[73] British Patent 323,765 (July 4, 1928); U.S. Patent 1,920,964 (Aug. 8, 1933).

[74] U.S. Patent 1,837,355 (Dec. 22, 1931).

[75] COATS, H. P., *Monthly Rev. Am. Electroplaters' Soc.*, **24**, 5 (1937).

[76] U.S. Patent 2,060,530 (Nov. 10, 1936).

[77] FISCHER, J., *Metallwirtschaft*, **11**, 473 (1932); BRAUN, A., *Oberflächentech.*, **12**, 39 (1935); NACHTMAN, J. S., *Steel*, **104**, 56 (June 12, 1939); BEHNKE, H., *Oberflachentech.*, **13**, 183 (1936); EGEBERG, B., and PROMISEL, N. E., *Metal Cleaning Finishing*, **9**, 577 (1937).

[78] HERMSDORF, R. P. E., and HEBERLEIN, MAX, *Trans. Am. Inst. Mining Met. Engrs.*, **121**, 289–298 (1936); DOWNIE, C. C., *Electrical Rev.*, **115**, 479 (1934).

[79] STOUT, L. E., BURCH, O. G., and LANGSDORF, A. S., *Trans. Am. Electrochem. Soc.*, **57**, 113 (1930).

[80] STOUT, L. E., *Washington Univ. Studies, Sci. and Technol.* (N.S.) No. 6, 9–37 (1932).

[81] FAUST, C. L., and MONTILLON, G. H., *Trans. Electrochem. Soc.*, **65**, 361

been deposited from cyanide baths and W alloys from alkaline solutions.[85]

In single metal deposition the possible codepositing cations are those of the metal and of hydrogen. It makes no difference whether most of the hydrogen discharged at the cathode escapes as gas. "Alloy" plating, as generally considered, merely changes this viewpoint to "hydrogen and two or more metals."

Microscopic examinations of sections of alloy deposits have revealed a "layer structure" apparently consisting of two different compositions.[86]

Alloy plating baths are generally of a type known to be suitable for depositing at least one of the metals in single deposition. A few examples are (1) Ni-Co,[87] Ni-Zn,[88] and Ni-Fe[89] from sulfate-chloride baths; (2) Cu-Zn,[90] Ag-Pb,[91] Ag-Cd,[92] Cu-Sn,[93]

(1934); **67**, 281 (1935).

[82] STOUT, L. E., and FAUST, C. L., *Trans. Electrochem. Soc.*, **60**, 271 (1931); **61**, 311 (1935).

[83] PROCTOR, C. H., *Metal Ind. (N.Y.)*, **18**, 13 (1920); MASAKI, K., *Bull. Chem. Soc. Japan*, **7**, 158 (1932).

[84] RAUB, E., and BIHLMAIER, K., *Mitt. Forsch.-Inst. Probieramts Edelmetalle staatl. höheren Fachschule schwäb. Gmünd*, **11**, 59–65 (1937).

[85] FINK, C. G., and JONES, F. L., *Trans. Electrochem. Soc.*, **59**, 461 (1931); HOLT, M. L., *Trans. Electrochem. Soc.*, **66**, 453 (1934).

[86] FAUST, C. L., HENRY, D. J., and FRANCE, W. G., *Trans. Electrochem. Soc.*, **72**, 479–500 (1937); FOERSTER, F., "Elektrochemie wasseriger Losungen," 3d ed., p. 376, J. A. Barth, Leipzig (1922); Discussion, *Trans. Electrochem. Soc.*, **73**, 414 (1938).

[87] WEISBERG, L., *Trans. Electrochem. Soc.*, **73**, 435 (1938); **77**, 223 (1940); *Steel*, **99**, 43 (July 13, 1936); GLASSTONE, S., and SPEAKMAN, J. C., *Trans. Faraday Soc.*, **26**, 565–574 (1930); **27**, 29–35 (1931); FINK, C. G., and ROHRMAN, F. A., *Trans. Electrochem. Soc.*, **58**, 416 (1930); FINK, C. G., and LAH, K. H., *Trans. Electrochem. Soc.*, **58**, 373 (1930); **72**, 458 (1937); YOUNG, C. B. F., and GOULD, N. A., *Trans. Electrochem. Soc.*, **69**, 585 (1936); KRONSBEIN, J., *J. Electrodepositors' Tech. Soc.*, **14**, 140 (1938).

[88] U.S. Patents 2,112,818 (Mar. 29, 1938); 2,114,006 (Apr. 12, 1938).

[89] THOMPSON, M. R., *Trans. Electrochem. Soc.*, **44**, 359 (1923); GLASSTONE, S., and SYMES, T. E., *Trans. Faraday Soc.*, **23**, 213–226 (1927); BURNS, R. M., and WARNER, C. W., U.S. Patent 1,837,355 (Dec. 22, 1931); NACHTMAN, J. S., *Steel*, **104**, 56 (June 12, 1939).

[90] COATS, H. P., *Monthly Rev. Am. Electroplaters' Soc.*, **24**, 5 (1937).

[91] FAUST, C. L., and THOMAS, B., *Trans. Electrochem. Soc.*, **75**, 185 (1939); *Metal Ind. (London)*, **55**, 253 (1939).

[92] FAUST, C. L., HENRY, D. J., and FRANCE, W. G., *Trans. Electrochem. Soc.*, **72**, 479–500 (1937).

[93] Intern. Tin Research Development Council, *Fourth General Report, Pub.* 95 (1939); HEUSSNER, C. E., *Am. Soc. Testing Materials*, p. 14 (April, 1938).

Au alloys from cyanide baths;[94] (3) Pb-Sn alloys from fluoborate baths;[95] (4) Al alloys from formamide solutions;[96] (5) Ni-Co alloys from triethanolamine baths.[97]

Since there are only a few metals having very similar activities in simple salt solutions, alloy plating baths are, for the most part, based on complex ion formation which provides relatively very low actual concentration of the metal ions. The metal ratio in the plate will probably differ from the ratio of "metal salts" in the bath.

Alloys of lead-thallium containing 20 to 65 per cent thallium are among the most insoluble alloys known. Fink and Conard[98] found that good, smooth, adherent deposits of an alloy containing approximately 70 per cent lead were obtained from a perchlorate bath of the two metals (30 g per liter thallium, 5 g per liter lead) at a current density of about 5 amp per sq ft (0.5 amp per dm²) and a temperature of 25°C.

Fink and Lah[99] obtained silver white deposits within the wide range of 55 to 75 per cent nickel and 45 to 25 per cent cobalt and the codeposition of these metals from a sulfate-chloride bath. Cobalt dissolves anodically more readily than nickel in the sulfate-chloride bath and also deposits cathodically more readily than nickel. Increasing the total metal concentration of the bath increases the cobalt content of the plate. An increase in the temperature of the bath, a decrease in the acidity, or an increase of the cathode current density likewise increases the cobalt content of the plate. The white alloy plate is more than three times as hard as nickel and decidedly more resistant to corrosion than nickel.

Nickel-copper alloys may be plated from baths containing mixtures of their cyanide complexes.[100] Studies of the deposits

[94] WEISBERG, L., *Trans. Electrochem. Soc.*, **73**, 431 (1938).

[95] BLUM, W., and HARING, H. E., *Trans. Electrochem. Soc.*, **40**, 287 (1921).

[96] BLUE, R. D., and MATHERS, F. C., *Trans. Electrochem. Soc.*, **63**, 231 (1933).

[97] BROCKMAN, C. J., and NOWLEN, J. P., *Trans. Electrochem. Soc.*, **69**, 553 (1936).

[98] FINK, C. G., and CONARD, C. K., *Trans. Am. Electrochem. Soc.*, **58**, 457 (1930).

[99] FINK, C. G., and LAH, K. H., *Trans. Am. Electrochem. Soc.*, **58**, 373 (1930).

[100] STOUT, L. E., BURCH, O. G., and LANGSDORF, A. S., *Trans. Am. Electrochem. Soc.*, **57**, 113 (1930); HINELINE, H. D., and COOLEY, W. B., *ibid.*, **48**, 61 (1925).

show that the percentage of copper in the plate is always greater than that of the bath, the difference becoming progressively greater as the copper content of the bath increases; the ratio of copper to nickel on the plate increases linearly with the temperature; and low current densities favor the deposition of high-copper alloys. Increase in free cyanide content was found to decrease the rate of deposition.

A number of special alloys are plated, some to a considerable commercial extent and others in only a very limited amount. Important among these are the nickel-iron alloys from sulfate electrolytes, particularly the valuable electrical permalloy. Certain of the precious metals are alloy plated for reflectors.

The alkali and the alkaline earth metals cannot be plated from aqueous electrolytes. The same holds true of magnesium and aluminum. The latter has been experimentally electroplated[101] from suitable organic complexes in ether solutions, complexes being of the Grignard type such as ethyl aluminum iodide. Multiple coatings of other metals on aluminum and procedures for these operations have been developed satisfactorily.[102] The platings are made on a roughened surface of aluminum and its alloys. Modifications of the general method of plating and surface preparation must be used when alloys of different compositions are plated.

Electrodeposition studies of a number of binary and ternary alloys are found in the literature, particularly cadmium-zinc,[103] thallium-zinc,[104] nickel-cobalt,[105] silver-cadmium,[106] iron-copper-nickel,[107] cadmium-zinc-antimony,[108] cadmium-zinc-tin,[109] copper-nickel-zinc.[110]

[101] KEYES, D. B., and SWANN, S., Studies in the Electrodeposition of Metals, *Univ. Illinois, Eng. Expt. Sta. Bull.* 206 (1930).

[102] WORK, H. K., *Trans. Am. Electrochem. Soc.*, **53**, 361 (1928).

[103] FINK, C. G., and YOUNG, C. B. F., *Trans. Electrochem. Soc.*, **67**, 311 (1935).

[104] PARKS, W. G., and LEBARON, I. M., *Trans. Electrochem. Soc.*, **69**, 599 (1936).

[105] YOUNG, C. B. F., and EGERMAN, C., *Trans. Electrochem. Soc.*, **72**, 447 (1937).

[106] FAUST, C. L., *et al.*, *Trans. Electrochem. Soc.*, **72**, 479 (1937).

[107] STOUT, L. E., and FAUST, C. L., *Trans. Electrochem. Soc.*, **61**, 341 (1932); **64**, 271 (1933).

[108] STOUT, L. E., and GOLDSTEIN, L., *Trans. Electrochem. Soc.*, **63**, 99 (1933).

Anodic Oxidation. Protective adherent oxide films can be produced anodically on aluminum and its alloys for protection against corrosion, for electrical insulation, for decorative effects, and for other uses. These can be dyed, painted, oiled, or otherwise treated. A number of different methods have been devised.

Whenever aluminum is made anode in a suitable electrolyte, an oxide film is produced on the metal. The properties of the oxide films are affected by many factors. Among these are the composition of the metal or alloy undergoing treatment, the constituents and their proportion in the electrolyte, as well as the temperature of the bath, and the electrical factors such as current and applied voltage. The color of the coating, its rate of formation, and its resistance to corrosion may be controlled by the composition of the metal.

The electrolytes proposed in the patent literature have been many and varied. Few of these have found industrial application. Among those proposed may be mentioned ammonium hydroxide, ammonium sulfide, borates, phosphates, tartrates, oxalates, and the corresponding acids, chromic acid, chromates, H_2SO_4 and sulfates, as well as many others. The applied voltages may vary from only a few volts to as high as 500 or greater. The colors of the coatings on aluminum metal itself may range from white to gray, depending upon how it was formed; on aluminum-silicon alloys it is gray to brown, and on aluminum-copper alloys it may have a greenish cast. The appearance of the coating will also be a function of the initial surface of the aluminum, which might be all the way from a highly polished metal to one with a sand-blast finish.

Some of the more important patents are listed below.

Chubb, U.S. Patents 999,749; 1,068,410; and 1,068,411, proposed the use of sodium silicate, ammonium borate, or other electrolytes. Mershon, U.S. Patent 1,065,704, used borax and boric acid for anodically coating aluminum cooking vessels to prevent sticking of food to the inside of pots. He states that electrodes for condensers and rectifiers may be made by the same process. Presser, U.S. Patent 1,117,240, insulated aluminum wire by anodic treatment in a bath of sodium carbonate.

[109] STOUT, L. E., and AGRUSS, B., *Trans. Electrochem. Soc.*, **66**, 441 (1934).
[110] FAUST, C. L., and MONTILLON, G. H., *Trans. Electrochem. Soc.*, **65**, 361 (1934); **67**, 281 (1935).

Abernathy, U.S. Patent 1,323,236, treated aluminum-coated copper wire in an aqueous solution of potassium permanganate and sulfuric acid. Flick, U.S. Patent 1,526,127, employed ammonia and ammonium sulfide as electrolyte. His patent gives a number of suggested proportions, as well as electrical conditions such as current density, voltage, and temperature. The material after anodic oxidation may be dyed by the use of acid dyes. The resulting compound is an aluminum salt of the dye acid, similar in nature to tinting pigments which are known as "lakes." Kujirai, U.S. Patent 1,735,286, proposed oxalic acid and oxalates as well as malonic acid. Bengough and Stuart, U.S. Patent 1,771,910, patented aqueous solutions of chromic acid free from H_2SO_4 and sulfates for the formation of coatings which are highly resistant to corrosion. Methods of this type have been widely used in protecting metal parts on aircraft. In British Patent 223,995 (1924), Bengough outlined a process for anodic oxidation and dyeing of the finished surface. He gives anthracene or anthraquinone blue as an example for the formation of blue colors, and alizarin red S for the production of reds. Gower, in British Patent 290,901 (1928), used an electrolyte containing H_2SO_4 or substances which give rise to H_2SO_4 at the anode. Coloring agents such as potassium dichromate, sodium hyposulfite, lead acetate, barium sulfite, and ammonium sulfocyanide, are suggested as additions to the bath to color or to tone the anodic deposit.

The methods which have found widespread use have been those with chromic acid electrolytes or H_2SO_4 electrolytes. The former are applied for the preparation of coatings which are highly resistant to corrosion, while the latter are employed for the development of colored aluminum finishes. The chromic acid method is a more expensive and time-consuming operation. The H_2SO_4 procedure is capable of rapid application in a simple manner with the usual plating equipment.

Bengough and his coworkers recommend a 3 per cent solution of chromic acid free from sulfates or H_2SO_4. The cleaned object as anode is subjected to a voltage which is gradually raised from 0 to about 50 volts over an hour's time. For airplane and dirigible parts, the time cycle is 0 to 40 volts in the first 15 min. The voltage is maintained at 40 volts for 35 min. It is then increased to 50 volts over a period of 5 min and maintained there for

another 5 min. The object is removed, washed, and dried in the usual manner. For maximum protection against corrosion, the oxide coating is strengthened or reinforced by the application of grease in thin layers.

The principal application has been the treatment of strong aluminum-alloy sheet. Operating data are given in Table 33. Copper-aluminum (Cu below 5 per cent), silicon-aluminum, and zinc-aluminum alloys coat readily, but in higher copper-content alloys the $CuAl_2$ constituent apparently prevents the formation of impervious films.

In the H_2SO_4 method, the electrolyte consists of dilute H_2SO_4 with small quantities of other chemicals to improve the properties of the anodic coating. The process may be divided into three stages: cleaning, anodic oxidation, and washing and dyeing. After cleaning, the piece is washed in water or in the case of some aluminum alloys, such as those containing copper, washed in dilute HNO_3. It is then hung as anode in the electrolytic cell. Operating data are given in Table 33.

In the electrolytic oxidation procedures, throwing power of the bath is not important nor are shaped cathodes required. The oxide film, which has an appreciable electrical resistance, first builds up on the portions of the anode nearest the cathode. There formation stops when the film resistance builds to a point where the electrolytic action is transferred to unoxidized surfaces. Eventually the whole object is covered with oxide.

Acid concentration of the electrolyte may be varied from 10 to 70 per cent and the time of treatment 10 to 15 min. By the selection of proper acid concentration, time of treatment, and voltage, it is possible to produce anodic films on aluminum and aluminum alloys, which films are flexible enough to withstand bending, pressing, deep drawing, stamping, and further fabrication. With other acid concentrations, treatment times, and higher voltages, very hard oxide films may be formed on fully manufactured products.

With pure aluminum, the film is almost colorless and transparent. With aluminum-silicon alloys, there is a tendency toward the development of gray shades. The metal underneath the film gives a metallic luster reflection.

Dyeing is usually done with aqueous solutions of organic dyestuffs, the dyeing being done immediately after the electro-

TABLE 33. ALUMINUM ANODIZING

	Sulfuric acid method		Chromic acid method
Anode...	Aluminum or aluminum alloy being treated		Aluminum or aluminum alloy being treated
Cathode:			
Material...	Lead		Graphite
Shape....	Flat sheet		Flat plates
Electrolyte:			
H_2SO_4, %..	10–70	15	
CrO_3, %......	. ...	.....	3
Temperature, °C..	15–20	25	40
C.d., amp/sq ft...	.....	. .	2–4[1]
Voltage.......	10–15	10–15	0–40 (15 min)
			40 (35 min)
			40–50 (5 min)
			50 (5 min)
Treatment time, min..........	10–15	.....	60
Power consumption, kwhr/sq ft	0 05–0.2		
Film thickness, mm...... ..	0.04 max.	. . .	0.00003–0.002, av. 0 0007[2]
Breakdown voltage:			
0.0075-mm film	. ...	230	
0.035–mm film....	. ...	475	

Other methods

	1	2	3	4
Boric acid, g/l	90			
Borax, g/l........	1.88			
Oxalic acid, g/l............... ...	....	5–10		
Phosphoric acid, g/l...... ...	....	.....	760–860	
Sulfamic acid, g/l.....	......	.....	......	48.75–100 5
Temperature, °C...............	93	29	29–32	49
Voltage range.......... ..	230–250	50–65	5–30	15–25
Voltage build-up..	....	Yes	Yes	Yes
C.d., amp/sq ft..........	10–40	10–30	10–20	6–25
Time for films 0.00001 in. thick, min	15			
Time for films 0.0001 in. thick, min.	....	20	5–15	15
Dye adsorption of film.............	None	Poor	Poor	Good

[1] SUTTON, H., and SIDERY, A. J., *J. Inst. Metals*, **38**, 241 (1927).
[2] SUTTON, H., and WILLSTROP, J. W. W., *J. Inst. Metals*, **38**, 259 (1927).

lytic treatment and washing. If the film be allowed to dry, microscopic pores in it become filled with air, and the dye solution does not readily penetrate. The dye baths are operated at 75 to 80°C (167 to 176°F), and the dyeing time is 10 to 20 min.) The articles are then washed until they no longer give up any dyestuff. The dyestuffs are believed to form "lakes" with the aluminum oxide and are thus precipitated in the film.

Other methods have come into use employing electrolytes of oxalic, phosphoric, sulfamic, and boric acid. Operating conditions are given in Table 33.

Metal Coloring. Although the common methods of metal coloring are distinctly chemical in nature, applied by rubbing, dipping, or dyeing methods, some electrolytic procedures have found industrial application. Craig and Irion[111] produced rapid patinas on copper and its alloys[112] by employing alkali carbonate electrolytes at current densities of 9 to 185 amp per sq ft with copper as anode to form basic carbonate coatings which were adherent and protective. Stareck and Taft[113] used alkaline solutions of copper lactate to produce Cu_2O anodic colors in a range of shades at current densities of 1.4 amp per sq ft at 0.25 volt. "Electrocolor"[114] uses copper anodes in a Cu^+ ion electrolyte to deposit Cu_2O in a wide range of colors whose shade and depth are a function of time and current density. On different metals violet, blue, green, yellow, orange, and red may be produced. Zinc may be anodically colored[115] in phosphates, ferro- or ferricyanides, permanganates, chromates, oxalates, and molybdates whose solutions are maintained at a pH of 6 to 8.[116]

Electroforming. Electroforming may be defined as the production or reproduction of articles by electrodeposition. It includes electrotyping which has as its object the reproduction of printers' setup of type, engravings, and medals; the reproduction of phonograph matrices; the manufacture of tubes and sheets by electrodeposition. In electrotyping the mold of the object to be reproduced is first made either in soft metals by pressure or in

[111] Craig, G. L., and Irion, C. E., *Metals & Alloys*, **6**, 35 (1935).

[112] U.S. Patent 1,974,140.

[113] Stareck, J. E., and Taft, R., British Patent 452,464.

[114] Trademark of United Chromium, Inc.; Stareck, J. E., U.S. Patent 2,081,121.

[115] New Jersey Zinc Co., D.R.P. 626,502, Feb. 27, 1936.

[116] New Jersey Zinc Co., D.R.P. 623,563, Dec. 28, 1935.

wax. In the latter case the mold is a nonconductor, but its surface is made conducting by the application of a graphite coating. The surface may also be made conducting as the result of a thin deposit of copper formed by a $CuSO_4$ solution (over a previously graphited object) out of which the copper may be precipitated by finely divided iron filings. The second method is employed because of the difficulties encountered with graphited surfaces where the deposition of metal from solution on this surface does not take place at once over all the surface, but the deposit grows from a point where contact is made. Lead molds coated with graphite are sometimes employed, although it is much more common practice to treat lead molds with a dilute chromate solution to produce a film of lead chromate, which permits subsequent separation. After formation, the electrotype "shell" is removed from the mold and filled with a low melting-point metal, such as the lead-tin alloy type, to give the piece rigidity and strength. For accurate reproduction the mold becomes a negative of the object to be produced. The mold itself may be formed by electrodeposition from the original master or object to be produced. Operating details are given in Table 34. This is an accurate method of reproducing a metallic surface. It is possible faithfully to reproduce by the electrodeposition of nickel, lines 0.00002 in. in width as well as smaller scratches just at the limit of visibility with present microscopic methods.

An example of the use of electrodeposited negatives is in the production of phonograph records. The original wax or metallic record on which the sound was recorded is first coated with graphite upon which copper is deposited to form a negative master matrix. From this one or more master records or positives are made by electrodeposition. These are the same as the original wax record save that they are of metal. They are used as positives for the production by electrodeposition of other metal negatives, termed "pressing matrices" or "working masters." These are employed as molding dies for the production of phonograph records themselves which are made of synthetic plastics. These working masters are sometimes nickel-plated, but best results are obtained by making the initial deposit nickel, which in turn may be chromium-plated to obtain a hard surface and increase their resistance to abrasion. Before the

deposition of one metal on another, the two to be later separated, mechanical or chemical films are produced which allow this separation to be made. Greases or graphite are applied for the mechanical films, while chemical films may be formed by the use of soluble sulfides, chromates of lead and silver, and, particularly in the phonograph industry for separating copper forms, a film of silver iodide.

Electrodeposition of iron has been applied to the preparation of iron powders, special iron for transformer cores and repair of worn machine parts, as well as printing plates and "surfacing" of plates for etchings. It has also been applied to the preparation of molds and dies particularly for rubber tires and related articles.[117]

Electrotyping.[118] In ordinary electrotyping work the electrolytes used are 8 to 10 per cent H_2SO_4 solutions nearly saturated with $CuSO_4$ at room temperature. Current densities are relatively higher than are used in plating, being of the order of 50 amp per sq ft (5.4 amp per dm^2) in ordinary work, and under favorable conditions, especially with addition agents, as much as 200 amp per sq ft (21.6 amp per dm^2) may be employed.

TABLE 34. ELECTROTYPING

Precoat:	
$\quad CuSO_4$	60 g/l (8 oz/gal)
$\quad$ Fe filings..	Dusted on wet waxed surface
Plating solution:	
$\quad CuSO_4$	255 g/l (34 oz/gal)
$\quad H_2SO_4$	75 g/l (10 oz/gal)
Anode-cathode spacing	10 cm (4 in.)
Current density	8–40 amp/dm^2 (74–370 amp/sq ft)
Average thickness of plating	0.018–0.020 cm (0.007–0.008 in.)
Agitation...	Air
Temperature.	38°C (100°F)

Seamless Tubing and Other Objects. Seamless copper tubes were first electrolytically produced by Elmore.[119] Cowper-Coles and the Société des Cuivres de France later published details of a process which is a modification of Elmore's. Seamless iron tubes

[117] *Ind. Eng. Chem., News Ed.*, **17**, 461 (1939).

[118] *Natl. Bur. Standards* (*U.S.*), *Circ.* 387; *Tech. Bull.* 19, Government Printing Office; *Tech. Bull.* 5, International Association Electrotypers and Stereotypers.

[119] ELMORE, C., *Electrochem. and Metall.*, **3**, 150 (1903).

have been introduced in sections of a few meters at the plant in North America as well as by Bouchayer and Viallet at Grenoble, France. The practice at these plants consists of depositing copper or iron in any desired thickness on a rotating mandrel which serves as cathode, then removing the tube from the mandrel. The mandrel surface is usually given a preliminary thin coating of some material to facilitate the removal of the tube, being freshly coated each time it is used as cathode in the cell. In removing the finished deposit, it is usually mechanically worked in order to increase the circumference of the tube slightly. In this respect great difficulty is encountered in producing small diameter tubes by this process, since they are not easily removed from the mandrel. In the case of the copper tubes the electrolyte consisted of acid $CuSO_4$ solution and the anodes were of cast copper, while in iron deposition $FeCl_2 \cdot 4H_2O$ electrolytes were employed with cast-iron anodes. The voltages and current densities were low. Various mechanical modifications were employed to produce dense and even deposits, such as burnishers held in place on the cathode surface by springs.

Billiter[120] has described two electrolytic methods for the production of continuous tubing of iron or copper. In the first method metal is deposited on a short, slightly conical mandrel of chrome or silicon steel (to which the deposit does not adhere), and at regular intervals the tube is moved slightly forward over the mandrel, thereby exposing a short bare section of mandrel. During the next time interval a new deposit forms over this exposed section as well as over the deposit produced during the previous interval. In the second method a low-melting hollow lead mandrel is slowly passed through a plating cell. After formation of the tube the mandrel is melted out.

Narrow flat copper tubing through which small supporting tubes pass transversely at regular intervals has been produced electrolytically by deposition on a suitably perforated lead band which passes continuously through the solution. After formation of the tube the lead is subsequently melted out.[121]

Very thin sheets, particularly of copper, have been formed by electrodeposition on a belt continuously moving through the solution, the product being taken off the belt where it passes out

[120] BILLITER, J., *Trans. Am. Electrochem. Soc.*, **57**, 131 (1930).

[121] *Met. & Chem. Eng.*, **12**, 67 (1914).

of the deposition tank. Extremely thin gold foils have been made in this manner by deposition on a belt of metallic silver. The process has limitations in that relatively thick deposits must be made to overcome porosity.

Shakespeare reported the development of continuous sheet copper by electrodeposition on a rotating drum cathode of lead.[122] The cathode moves slowly at such a rate that metal of the desired thickness is deposited, stripped off the cathode above the solution line, washed, dried, and taken up. Lead anodes are spaced about ½ in. from the drum, the electrolyte being acidified $CuSO_4$ circulating through the lead-lined concrete tank. Anode gas evolution provides agitation, supplemented by compressed air supplied through the ends of the anodes under the center of the drum.

Operating details are not available, but pilot-plant data are given in Table 35. The arrangement of the drum in the tank is shown in Fig. 60, showing the location of the polishing brush to continuously renew the cathode surface. O'Brien[123] states that the commercial drums are 85 in. in diameter by 64 in. wide, allowing the production of sheet almost as wide as the cathode face, in weights of less than 1 oz to more than 7 oz per sq ft.

TABLE 35. PRODUCTION OF ELECTROLYTIC SHEET COPPER

Electrolyte.	Acidified $CuSO_4$
Means of circulation..	Gas ebullition at anodes, plus compressed air under center of drum
C.d., amp/sq ft cathode.	140–190
Voltage...... .	2 0–2.8
Ampere efficiency, %.. .. .	95
Kwhr/lb Cu........... .	1 25
Pounds Cu per kwhr... . .	0 8
Anodes:	
Material.......	Lead
Changed after ? days..	365
Anode-cathode spacing, in . . .	0.5
Cathodes:	
Material...................	Lead
Shape.................	Revolving drum
Per cent scrap.....	15–20
Tank material.....	Concrete, lead-lined

[122] SHAKESPEARE, W. M., *Trans. Am. Inst. Mining Met. Engrs.*, **106**, 441 (1933).

[123] O'BRIEN, A. L., *Metal Ind.* (*N.Y.*), **36**, 218 (1938).

Sheet zinc can be produced in a similar fashion from a $ZnSO_4$ electrolyte and aluminum cathodes.

Dies[124] for molding rubber, glass, and plastics are prepared by depositing iron on rubber and rubber composition molds. Deposits of 2.5 cm (1 in.) in thickness are not unusual. Dies for buttons, brush handles, tire casings, radio dials, leather and
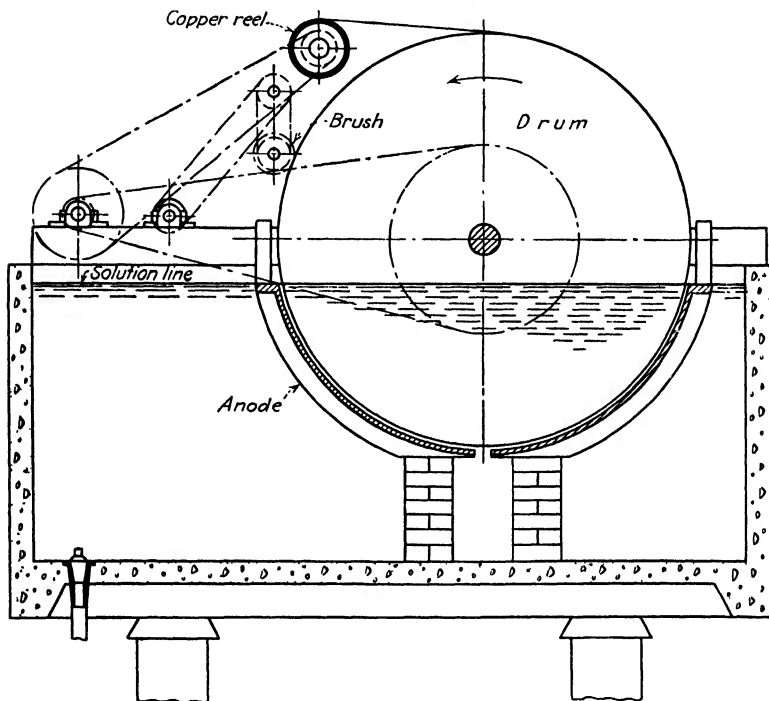
Fig. 60. Sectional elevation of drum equipment.

wood-grain stamping dies, glass molds, etc., comprise a small number of the many articles being manufactured by electroforming.

Duplicate intaglio printing plates[125] used for printing paper currency are manufactured at the U.S. Bureau of Engraving and Printing in Washington. The process involves the deposition of nickel, iron, and chromium. A metal mold or alto is first pre-

[124] Bull, A. W., Bishop, J. W., Orbaugh, M. H., and Wallace, F. H., *Ind. Eng. Chem., News Ed.,* **17,** 461 (1939).

[125] Thomas, C. T., and Blum, W., *Trans. Am. Electrochem. Soc.,* **57,** 59 (1930).

pared from the original, following which a replica of the original or basso (printing plate) is made from the alto (mold).

Metal screen[126] is made continuously on a rotating drum cathode. Principally nickel and copper are deposited. Sheets 9.2 dm (36 in.) wide and 1,400 ft. long have been produced. The product is used as carburetor screens, screen fabric for radio loud-speakers, etc.

Clock dials, tubes, pipe fittings (such as ells, tees, etc.), art objects of a wide variety, embossing dies (artificial leather, fabric, wood grain, etc.), machinery parts, bells for musical instruments, seamless copper tanks for water heaters, float balls, parts for pressure gages, and transformer cores are manufactured by electroforming.[127]

Metal Powders. A large number of articles are now made by powder metallurgical methods whereby metal powders or mixtures are compressed in dies and the molded pieces sintered. A large proportion of the powders for these uses are the product of the electrolytic refining tank where, with high current densities and specifically controlled electrolytes, nonadherent cathode deposits of more or less controlled shape and size are produced. The method competes economically with mechanical disintegrating processes and the treatment of oxide powders by reducing gases. The electrolytic procedure has been applied to a wide range of metals. In some cases brittle cathode deposits are produced which are later processed mechanically.

Rossman[128] abstracted the literature on metal powder production. In practice, cathode current densities are higher than those of refining, so that loosely adherent spongy deposits which are periodically removed by scraping or tapping devices or by electrolyte circulation may be produced. In the case of copper powder, acid electrolytes of lower metal and higher acid concentration than those used for refining or plating are preferred. When operated at high cathode current density and with hydrogen evolution, the finely divided metal crystals often have a

[126] *Inco* (International Nickel Company house organ, N.Y.), **16**, 20 (No. 4) (1939); BEEBE, W., U.S. Patents 2,225,733–4 (1940); NORRIS, E. O., U.S. Patents 2,226,381–4 (1940).

[127] WEIN, S., *Product Eng.*, **10**, 486 (1939); *Proc. Am. Electroplaters' Soc.*, **26**, 271 (1939).

[128] ROSSMAN, J., *Metal Ind.* (*N.Y.*), **30**, 321, 396, 436, 468 (1932).

fernlike appearance under the microscope. It is necessary to remove the cathode frequently; otherwise the effective area of the deposit will be increased to such an extent that the current density will be lowered and coarse deposits formed.

The fineness of the powder may be varied over a considerable range by changes in the composition, temperature of the electrolyte, and variation of the cathode current density, as well as by the introduction of addition agents, reducing compounds, or substances which are cathodically reduced and anodically oxidized but are not plated out. It is common practice to use cathode current densities which are different from those at the anode, usually higher. The deposited powders are thoroughly washed, dried in inert or reducing atmospheres, and cooled to room temperature. Copper, zinc, iron, cadmium, tin, antimony, and silver powders are produced electrolytically in large quantities, while many other metal powders are produced by electrochemical means in smaller amounts.

French electrolytic copper powders were produced through the addition of colloidal materials, such as H_2SO_4-treated glucose, for example, to the electrolyte.[129] The colloid was thought to make possible the production of extremely fine powders with the elimination of hydrogen evolution at the cathode and higher current efficiencies. American production of copper powder avoided these additions and made the material in modified refining tanks from selected regular anodes and smooth copper cathodes. After washing, drying, and screening, oxygen content is removed by hydrogen or gaseous reduction.

Mantell described the preparation of copper-coated lead powder using an acetate electrolyte with copper and lead anodes and nickel cathodes at cathode current densities of 18 amp per sq ft at a power consumption of 1.5 kwhr per lb of 200-mesh powder containing 60 per cent copper and 40 per cent lead.[130]

Electrolytic zinc powder is made from flue dust with a caustic leach liquor and an electrolyte of sodium hydroxide and sodium zincate. The product shows a typical fern-leaf appearance of sizes 45 to 60 microns long. Zinc dust is employed as a reducing agent in the manufacture of hydrosulfites and in the preparation

[129] U.S. Patent 1,799,157; British Patent 303,984; French Patents 349,459 (1905); 511,428 (1920); 656,777.
[130] U.S. Patent 2,182,567 (Dec. 5, 1939).

TABLE 36. OPERATING DETAILS—ELECTROLYTIC ZINC AND NICKEL POWDERS

	Electrolytic zinc powder	Electrolytic nickel
Raw material	High-grade Zn flue dust	Nickel
Cell:		
Material of construction......	Steel, rubber-lined	Steel, rubber-lined
Capacity, lb/day.	110	
Electrolyte:		
Electrolyte feed.	200 g/l NaOH, 10 g/l Zn	300 g/l NH_4Cl, 2 g/l NaOH
Electrolyte effluent. . . .	200 g/l NaOH, 9 g/l Zn	
Temperature, °C.. .	30	23–26
Method of feed . . .	Gravity	
Circulation method	Rubber-lined pump	
Current:		
Current per cell, amp.. .	2,500	
C.d. anode, amp/sq ft ...	. . . .	10–20
C.d. cathode, amp/sq ft.. .	120–150	20–30
Current efficiency, %.....	80–90	55
Volts per cell....... .	3.4	1.4–1.5
Power consumption:..... . ..		
Kwhr per lb metal...........	1.37	1.13
Lb metal per kwhr...	0.73	0.88
Anode....	Ni sheet	Nickel
Cathode.....	Hollow iron or Mg alloy (Elektron)	Sheet nickel
Electrode spacing... ...	1.18 in. (30 mm)	1.5 in.
Final product, % metal	Paste 35–45 Zn, dry dust 85–95	98–99

of organic compounds. Commercial operating data of a plant employing hollow magnesium alloy cathodes are given in Table 36.

Electrolytic nickel has been made by Mantell[131] employing an ammonium chloride electrolyte whose pH was adjusted by means of sodium hydroxide, using nickel anodes and nickel cathodes. Operating details are given in Table 36.

[131] MANTELL, C. L., U.S. Patent 2,233,103 (Feb. 25, 1941).

CHAPTER 15

ELECTROREFINING OF METALS

In 1800 Cruikshank called attention to the fact that metallic copper could be precipitated from its solutions by means of the current of Volta's pile. Faraday's fundamental laws of electrolysis came in 1831, and Jacobi's book[1] in 1835 described practical applications. His "galvanoplasty" was invented in 1838. Elkington started an electrolytic silver-plating plant in Birmingham in 1840–1841. During the years 1865–1870, shortly after the development of the dynamo, James Elkington's patents on electrolytic refining of copper were published, and the art was brought into being. The processes were described with such completeness that the specifications are still interesting reading.

It is interesting to note that, while the invention of the dynamo made possible the electrolytic refining of copper, the pure copper thus produced opened up the great electrical industry of today with a steadily increasing annual consumption of copper. The two industries are naturally dependent upon each other and have had a parallel growth. The first refinery in the United States was built by Edward Balbach in 1883 at Newark. Under the leadership of the Balbachs and Thums this plant became noted for electrochemical pioneer work, not only in copper, but in silver, gold, and nickel as well. It operated continuously until 1918 when the tank house was dismantled.

COPPER

Electrolytic refining of copper not only produces the exceedingly pure grade of copper demanded by the electrical industry, but it also recovers the small quantity of precious metals present in the original ore which could not be recovered by any other process. Crude copper contains precious metals such as gold, silver, and platinum, as well as nickel, arsenic, antimony, sele-

---

[1] JACOBI, P., "Application de l'électromagnétisme," Potsdam, 1835.

nium, tellurium, and other metals as impurities. A weighted average analysis of the crude copper handled by commercial refining plants indicates that the amount of gold is of the order of 375 oz (23.4 avoirdupois pounds) per million pounds of copper, the silver 25,000 oz (1,560 avoirdupois pounds) per million pounds of copper, the platinum 0.5 to 1 oz per million pounds of copper, and a greater quantity of palladium than platinum. A Montana ore, for example, contains about 0.6 oz of silver for every percentage of copper present, or about 2 oz of silver per ton of average ore smelted. The gold value may be expressed only in cents per ton of ore. So large is the tonnage of ore handled, however, that Montana is among the largest silver-producing states of the country. Silver and gold are recovered out of ores so lean in precious metals that the ores would not have been workable for silver and gold alone.

During the smelting of copper and lead ores, the base metals act as a carrier for the precious metals which are to be found in the crude copper and lead. About 75 per cent of the total silver production of the world is recovered as a by-product of copper and lead refining.

The raw material for refining is "blister," the product of the copper blast furnace; or "cement copper," the finely divided and granular material recovered from solution by precipitation with metals like iron or detinned tin-plate scrap; copper cakes, or scrap in various forms and purities. For the average refinery the major share of the crude copper is blister.

As a liquid metal solidifies, the impurities, including silver and gold, tend to remain liquid and concentrate in that portion of the metal which solidifies last. Consequently there is considerable segregation of the precious metals in the blister copper slabs. It is necessary that the samples represent the entire surface of the slabs. To obtain a representative sample, the "template" method of drilling is employed. This consists of marking the surface of the slab into inch squares and sampling each slab in a different square, so that when completed the drillings represent samples from each square and from both sides of the slab. The drillings, after thorough mixing, are ground and divided into three parts: one each for the seller, the buyer, and the umpire in case of dispute.

The flow sheet of a copper refinery, as the result of by-products

and recoveries, is complicated, as shown by Fig. 61,[2] but becomes more so when selenium and tellurium are also recovered.

Anodes. The blister copper comes to the refinery in the form of slabs about 28 by 18 by 3 in., weighing 350 lb. From the boats or railroad cars they are transferred to industrial cars and carefully checkweighed on duplicate scales. The slabs are then sent to the sampling mill where a certain percentage of them, deter-

INCOMING BLISTER COPPER — SCALES — DRILL ROOM — ANODE FURNACE — ANODES — TANK HOUSE ELECTROLYTIC TANKS — CATHODES

SMELTER — SLAG — IMPURE SOLUTION — ANODE SCRAP — CATHODE SCRAP

SLIMES CONTAINING Au, Ag, Pt, Pd and Se — SOLUTION — SILVER REFINERY — SETTLING TANKS — SLIMES — ROASTER FURNACE — LEACH TANKS — CENTRIFUGE — DRIED LEACHED SLIMES

ACID-RECOVERY PLANT — SLAG — LIBERATOR TANKS — LIBERATOR COPPER — DE-COPPERIZED SOLUTION — FURNACES, ANODE AND WIRE BAR — EVAPORATOR — PRECIPITATING TANKS — RECLAIMED ACID — NICKEL RESIDUE — SETTLING TANKS — TANK HOUSE ELECTROLYTE — MARKET

WIRE-BAR FURNACE — REFINED COPPER — CASTING WHEEL — WIRE BARS INGOTS INGOT BARS CAKES — MARKET

SHEAR — CUT CATHODES — MARKET

DORÉ METAL — DORÉ FURNACE — LOW GRADE SLAG — PARTING CELLS — FINE SILVER CRYSTALS — GOLD MUD — DIGESTERS — SILVER CHLORIDE SOLUTION CONTAINING Au, Pt and Pd — PRECIPITATING TANKS — GOLD SAND SOLUTION Pt, Pd

CRUCIBLE — SILVER BARS — MARKET — REDUCTION — SILVER RESIDUE — TO DORÉ FURNACE — CRUCIBLE — ANODES — WOHLWILL CELLS — CATHODES — CRUCIBLE — GOLD BARS — MARKET — Pt, Pd CONCENTRATE — WASHED DRIED AND GROUND — Pt METALS PLANT — PRECIPITATING TANKS

FIG. 61. Flow sheet, Ontario Refining Co., International Nickel Company of Canada.

mined by the silver content, are drilled and sampled. The refineries are held strictly accountable for the various metal values in the blister copper. Blister slabs are melted in large reverberatory furnaces of 250- to 400-ton capacity. Generally no attempt is made to purify the copper from base metals, only the oxygen and sulfur being removed. Secondary copper-bearing materials are usually subjected to preliminary furnace refining. The crude copper is cast in the shape of anodes, the

[2] BENARD, F., *Trans. Am. Inst. Mining Met. Engrs.*, **106**, 373 (1933).

Fig. 62. Effect of impurities on the conductivity of copper.
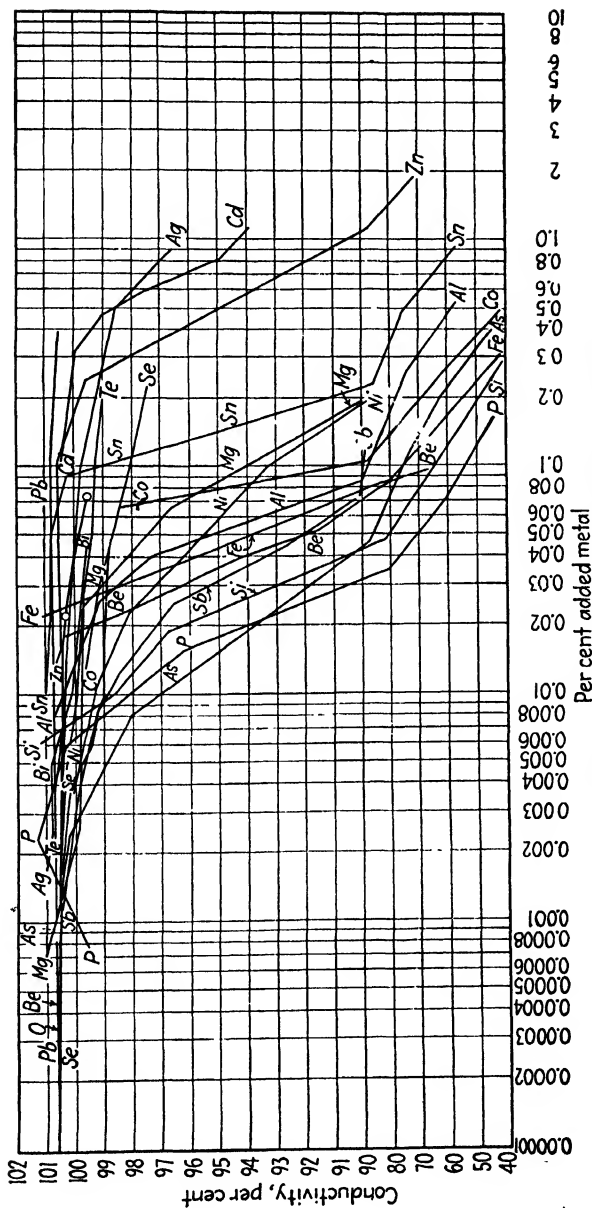
sizes varying in the different refineries. In the multiple system they weigh from 500 to 770 lb. They are cast with as smooth a surface as possible to avoid short circuits in the electrolytic tanks. All multiple-system anodes are cast with lugs not only for suspension purposes but to carry the current, one lug resting directly upon the bus or triangle bar. In comparison with most metals which are termed "crude," copper anodes are relatively pure, being 99 per cent to 99.5 copper. Typical analyses for the anodes refined in the major plants of the world are given in Table 37. The effect of impurities on the conductivity of copper as given by Skowronski[3] is summarized in Fig. 62.

Systems of Refining. There are two systems of electrolysis in use today: the multiple system, sometimes called after Elkington, used in most of the refineries, and the series system, also known as Hayden.

In the multiple system the anodes and cathodes are arranged in the tank in parallel, requiring a cathode starting sheet on which the copper will deposit and busbar connections between the individual anodes and cathodes. In the series system only the two end electrodes are connected with the circuit. The others, 100 to 150 in number, are placed in the tanks, acting as bipolar electrodes of which one side, as anode, goes into solution, the other side, as cathode, receiving the pure metal deposit. Both systems have disadvantages as well as advantages, but, owing to its greater flexibility, the multiple system is more generally used. The series system is dependent on pure anodes, very carefully made. The anodes are cast by hand, or they are rolled. The multiple system will be described in detail.

Current Density. The current density used is the most important factor in copper refining. Starting at first with 3 to 5 amp per sq ft (0.32 to 0.54 amp per dm^2) of cathode surface, it has gradually increased until one plant with cheap power used at one time as high as 40 amp per sq ft (4.3 amp per dm^2). Operating data of the major refineries of the world in Table 38 indicate a cathode c.d. range of 15 to 33 amp per sq ft, with most of the refineries operating between 15 and 18, except where power is quite low in cost. Figure 63 shows the approximate relationship

---

[3] Skowronski, S., Private communication. See also Wyman, L., *Gen. Elec. Rev.*, **37**, 120 (1934).

between current density and power cost.[4]   The same figure indi-
cates the effect of increased current density on the carry-over of
gold and silver from the anodes to the cathodes, which is stated
as the percentage of gold and silver in the anodes lost in the
cathodes.   The losses of precious metals and their transference
to the cathodes are affected by the amount of silver in the anodes,
which factor may be more important than current density.   The
lower the density, the better the grade of cathode copper and
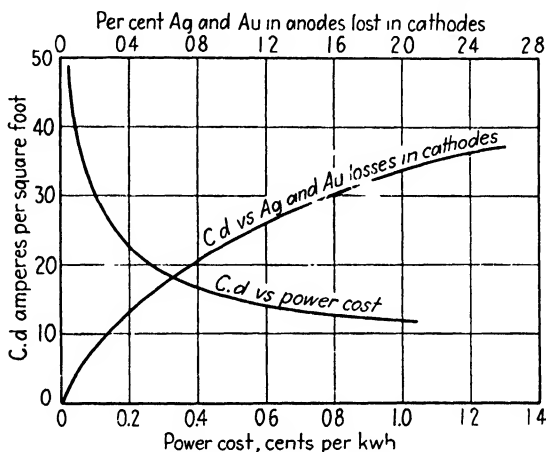
Fig. 63.   Current density *vs.* power costs and precious metal losses in cathodes.

the cheaper the power cost of electrolysis.   To offset this, how-
ever, a plant of larger size is required, and a larger amount of
capital is tied up, both in equipment and in metals.   The required
power equipment varies as the square of the density used, and
the power input increases inversely in proportion to the density,
for power $= I \times E$ and $I = E/R$.   With 15 amp per sq ft
(1.6 amp per dm^2) 10 lb of copper per kilowatthour can be
obtained in plant operation, while with 20 amp per sq ft (2.2 amp
per dm^2) only 7.5 lb of copper will be produced.   The current
used by any refinery is the economic equilibrium between the
cost of power and the cost of building plant and equipment and
the interest on metal tied up.

   In Fig. 64 the relations between current density and cell volt-
age of the various producing plants whose operating details are

---

[4] ADDICKS, L., "Copper Refining," pp. 61, 65, McGraw-Hill Book Com-
pany, Inc., New York, 1921.

TABLE 37. COMPOSITION OF ANODES USED IN ELECTROREFINING OF COPPER

	Cu, %	Ag, oz/ton	Au, oz/ton	Pb, %	Sb, %	As, %	Se, %	Ni, %	Te, %	Fe, %	Co, %	Zn, %	Bi, %	S, %
American Smelting & Refining Co., Barber, N.J.	99 0	95 0	1 5	0 02	0 006	0 0076	0 009	0 038						
American Smelting & Refining Co., Baltimore, Md.	99 25	73 5	1 75	0 03	0 05	0 06	0 06	0 08	0 01					0 007
American Smelting & Refining Co., Tacoma, Wash.	99 2	70–90	4 0–5 0	0 06	0 05	0 08	0 04	0 14		0 05				
Anaconda Copper Mining Co., Great Falls, Mont.	99 35	30	0 30	0 02	0 030	0 05	0 020	0 030	0 035	0 0012		0 0010	0 008	0 0024
Canadian Copper Refiners, Ltd., Montreal East, Que.														
Noranda anodes	99.37	23 79	4 274	0 0004	0 0001	0 0012	0 144	0 017	0 027	0 0013				0 0065
Hudson Bay blister	98 95	39 80	2 731	0 035	0 0045	0 015	0 117	0 009	0 015	0 0013				0 031
International Nickel Company of Canada Ltd., Copper Cliff, Ont.	99 17	3 79	0 694	0 005	0 01	0 005	0 058	0 48	0 006	0 001				0 12
Mt. Lyell Mining & Railway Co. Ltd., Queenstown, Tasmania	99 21			0 0073	0 0083	0 0019	0 021	0 0195	0 0093	0 042	Trace	Trace	Less than 0 0001	
Norddeutsche Affinerie, Hamburg, Germany														
Phelps Dodge Refining Corp., El Paso, Tex.	98.8 / 99 57	35 5 / 25 5	0 9 / 0 81	0 021	0 0033	0 0032	Se and Te 0 028	Ni and Co 0 631		0 004	Ni and Co 0 631			0 0026
Phelps Dodge Refining Corp., Laurel Hill, N.Y.	99 20–99 60	10–48	0 2–1 0	0 02–0 12	0 01–0 06	0 03–0 14	Se and Te 0 02–0 17	Ni and Co 0 06–0 27		0 01–0 0026	Ni and Co 0 06–0 27			
Raritan Copper Works, Perth Amboy, N.J.	99 53	8 59	0 21	0 038	0 020	0 033	0 033	0 037	0 013	0 011		0 003	0 002	0 004
Rhodesia Copper Refineries Ltd., Nkana, Northern Rhodesia	99 75			0 200	0 0002	0 0011	0 0141	0 0154	0 0019	0 0050	0 0060		0 0045	
Société Général Métallurgique de Hoboken Belgium	93	29–61	0 01–0 30		0 025	0 17	0 01	0 15		0 002	0 001			
U.S. Metals Refining Co., Carteret, N.J.	99 25–98 90	50–120	1 25–3 0	0 18	0 11	0 05	0 074	0 15	0 045	0 03	..	0 005	0 002	

tabulated in Table 38, as well as power consumption per pound of copper, are plotted. The figures have been taken from Table 38. With increasing current density, cell voltage rises, and the power consumption per pound of copper increases. All the variables in the individual plants as they affect current density and power consumption are included, so that the curves represent trends for the entire industry and are not so regular as those curves obtained for the specialized conditions in individual plants. Inasmuch as the kilowatthours per pound of copper is inversely related to the energy efficiency, it is evident that with increased current density the energy efficiency decreases.
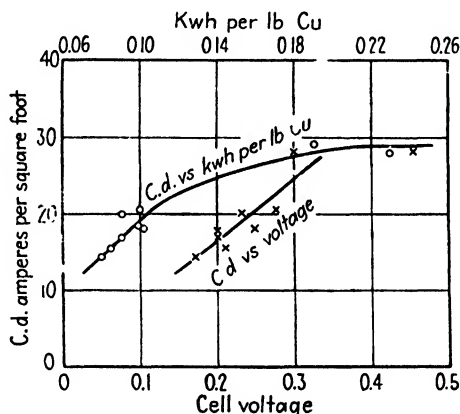
Fig. 64. Current density *vs.* voltage and power consumption in copper refining.

Electrolyte. The voltage per tank will vary with the current density and will depend upon the resistivity of the solution. The electrolyte commonly used today is 16 to 18 per cent free H_2SO_4 and 3 per cent copper at 55°C. The higher the acid content, the lower the resistivity of the solution and the lower the solubility of copper sulfate as well. Copper, nickel, and ferrous sulfates increase the resistivity of the solution. Successful electrolysis, however, is dependent upon a constant supply of copper ions at the cathode; otherwise hydrogen will be generated with a lowering of the efficiency. Moreover, as the copper dissolves at the anode, the solution in its immediate vicinity is always supersaturated, and copper sulfate will crystallize on the electrode if the acid content be too high. As a result, the anode will cease to function as a soluble anode and will act as an insolu-

ble one, raising the voltage and cutting down the copper content of the electrolyte. Circulation of the solution is therefore important to ensure the presence of copper ions at the cathode. Care must be taken at the same time to avoid stirring up the slimes containing the precious metals. A circulation of 4 gal per min is common practice at the refineries.
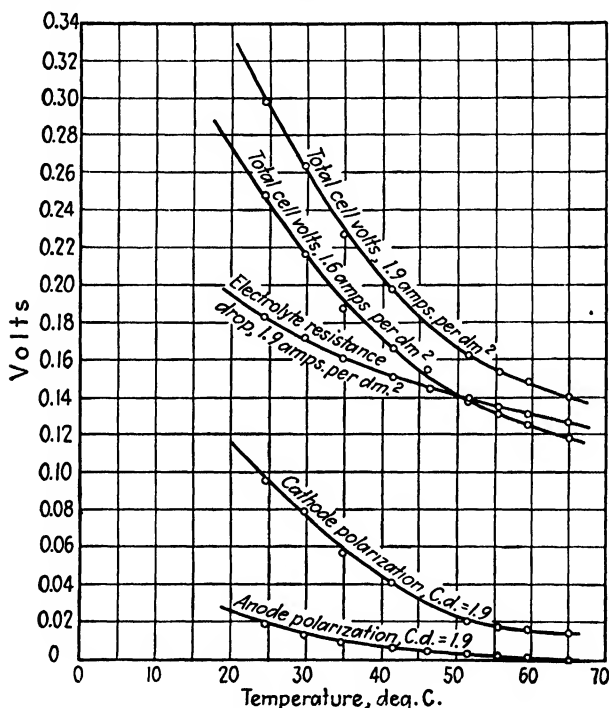
Fig. 65. Multiple refining system. Electrolyte analysis, grams per liter: H_2SO_4, 185.5; Cu, 42.0; Fe, 0.5; Ni, 14.8; As, 3.8. Anode face to cathode face = 4 cm. Current density = 17.65 amp per sq ft.

Kern and Chang[5] found that arsenic, nickel, and iron in $CuSO_4$-H_2SO_4 electrolytes decreased conductivity. They recommended an electrolyte of 30 to 35 g per liter Cu and H_2SO_4 up to 175 g per liter, operated at 55°C with iron and nickel kept as low as possible. Fink and Philippi[6] stated that high temperature

[5] Kern, E. F., and Chang, M. Y., *Trans. Am. Electrochem. Soc.*, **41**, 181 (1922).

[6] Fink, C. G., and Philippi, C. A., *Trans. Am. Electrochem. Soc.*, **50**, 267 (1926).

and H_2SO_4 up to 200 g per liter reduce the anode and cathode polarization and IR drop of the electrolyte, while increase in $CuSO_4$ content decreases polarization at the electrodes but increases the IR drop. Gelatin additions greatly increase the
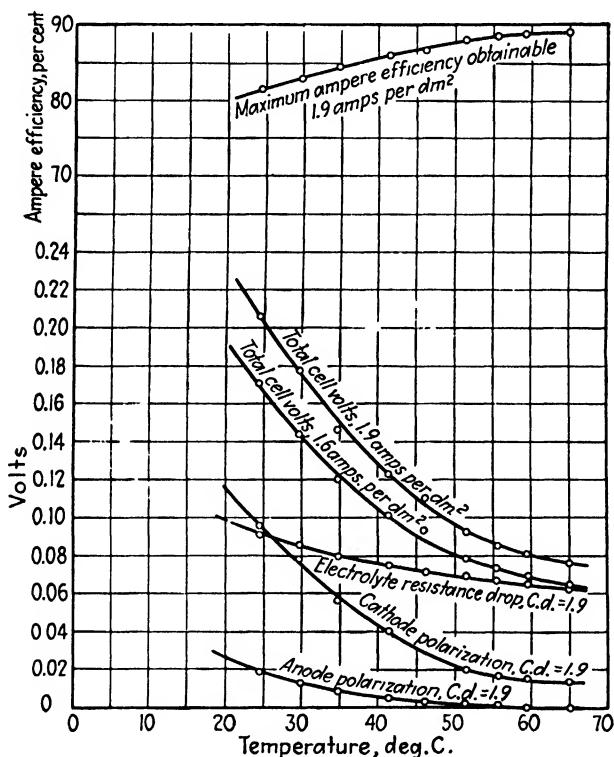
FIG. 66. Series refining system. Electrolyte analysis, grams per liter: H_2SO_4, 185.5; Cu, 42.0; Fe, 0.5; Ni, 14.8; As, 3.8. Anode face to cathode face = 2 cm. Anode thickness = 0.75 cm. Area of electrodes = 40 dm². Area of electrolyte below electrodes = 5.5 dm². Current density = 17.65 amp per sq ft.

cathode polarization but do not affect anode polarization or the IR drop through the electrolyte. Rouse and Aubel[7] analyzed copper-refining cell voltages for both the multiple and series systems. The effects of temperature on the various factors are given in Figs. 65 and 66. The effect of copper and glue is shown

[7] ROUSE, E. W., and AUBEL, P. K., *Trans. Am. Electrochem. Soc.*, **52**, 189 (1927).

in Figs. 67 and 68. Skowronski, and later Rouse and Aubel,[8] found no indication of a decrease in either the anode or cathode potential with the addition of varying amounts of nickel to the electrolyte. Chlorine acts as a cathode depolarizer and there-
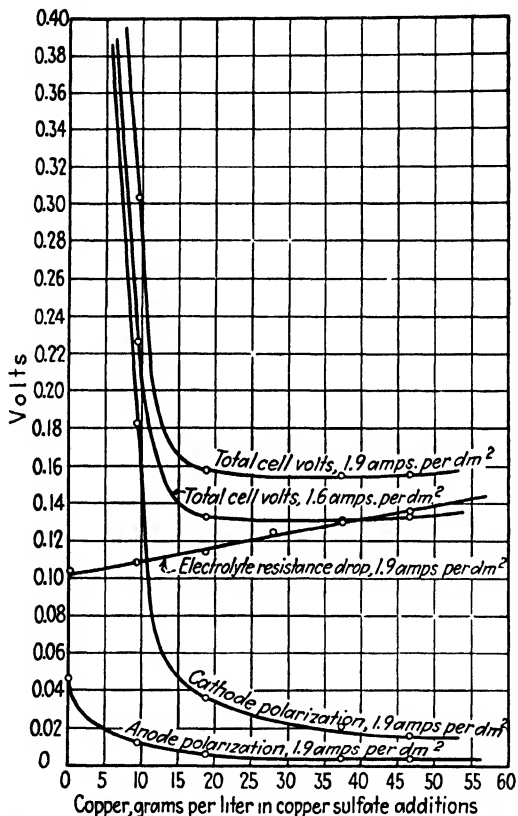
FIG. 67. Multiple refining system. Electrolyte analysis, grams per liter: H_2SO_4, 185.0; Fe, 0.5; Ni, 15.0; As, 3.8. Temperature of electrolyte = 57°C. Anode face to cathode face = 4 cm. Current density = 17.65 amp per sq ft.

fore serves as both an electrical and chemical agent. Rouse states that chlorine acts upon the electrode surfaces, in that tank-house experience shows that crystal size of deposits made in solutions containing 0.02 g per liter of chlorine are larger than the crystal size from an electrolyte containing only 0.005 g per

[8] Rouse, E. W., and Aubel, P. K., *Trans. Am. Electrochem. Soc.*, **52**, 201 (1927).

liter. For a specific electrolyte of H_2SO_4 and $CuSO_4$ containing sulfates of nickel, ferric and ferrous iron, arsenic, chlorides, as well as other materials, the addition of constituents which increase the resistivity also decreases polarization up to a limited point, beyond which further increases in concentration increase polarization.

Glue when added to the electrolyte tends to form colloidal films on the electrode surfaces. At the cathode copper must be
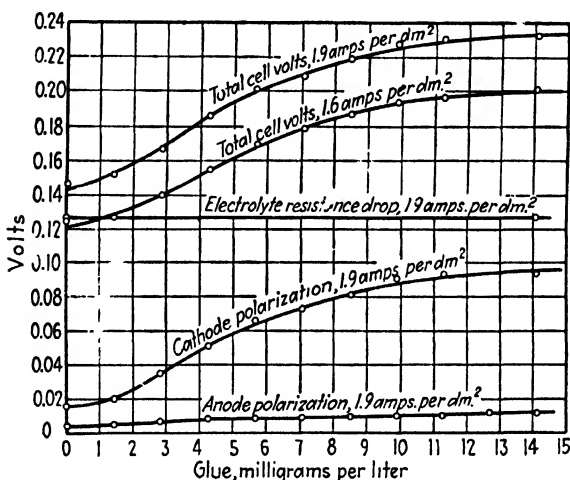
Fig. 68. Multiple refining system. Electrolyte analysis, grams per liter: H_2SO_4, 185.5; Cu, 42.5; Fe, 0.5; Ni, 14.8; As, 3.8. Temperature of electrolyte = 57°C. Anode face to cathode face = 4 cm. Current density = 17.65 amp per sq ft.

deposited upon the film there, which causes a large increase in cathode polarization, and a reduction in crystal size. At the anode the colloidal film need only be pushed away by the electrochemical solution of the copper, so that only a small increase in anode polarization occurs.

Skowronski and Reinoso[9] proposed a formula for calculation of electrolyte resistivity as affected by copper, nickel, iron, and arsenic, 1 g per liter of each of these elements in the form of sulfates increasing the resistivity of 150 g per liter H_2SO_4 at 55°C by the following percentages:

[9] Skowronski, S., and Reinoso, E. A., *Trans. Am. Electrochem. Soc.*, **52**, 205 (1927).

		Per Cent
Copper	. . . .	. 0.657
Nickel	. .	. 0.766
Iron ..	. . . .	0.818
Arsenic	.	0.0725

Voltage and Power. Tank voltages vary as a function of current density, tank construction, bus systems, and plant maintenance from as low as 0.17 to as high as 0.46, the usual plant running between 0.2 and 0.25. The voltage for refining is small as the result of the energy generated at the anode by the solution of the copper. For minimum voltage the anodes are spaced in the tanks as closely as possible. Some plants operate with a center to center spacing of $3\frac{1}{2}$ in., but perhaps the greater number operate with a center to center spacing from 4 to $4\frac{1}{2}$ in. Tanks are under continuous inspection for short circuits and bad contacts.

Sufficient tanks are connected in series so that generators in the voltage range of 80 to 235 are employed, the average plant, perhaps, operating in the range of 100 to 150 volts. In some of the newer plants generators with a wide voltage range have been installed, so that there is a large amount of flexibility.

Tank loads are of the order of several thousand to as high as 15,000 amp. The amperage follows Faraday's law, copper acting as a divalent metal. At 100 per cent efficiency, 1 amp per hr deposits 1.186 g of copper, equivalent to 1 oz of copper per ampere-day. In practice several hundred to as high as 800 tanks are connected in series. Busbar loads in some plants where power is cheap are above 1,000 amp per sq in. cross section, but the average for the industry is probably closer to 500 amp per sq in. cross section. Current efficiencies in the multiple system are above 90 per cent, some refineries reporting as high as 98 per cent, while in the series system they are of the order of 70 to 75 per cent. Further details are given in Table 38.

Plant Operation. Some typical plant practices are given in brief. The tanks were formerly of wood, generally long-leaf yellow pine, covered with sheet lead containing 4 per cent antimony and weighing 6 lb per sq ft. The modern tendency is to use lead-lined concrete tanks. They are connected in series by means of the Walker system where the anode of one tank rests upon a common contact or busbar with the cathode of

the adjoining tank, thus effecting an important saving in the total weight of copper tied up in busbar connection. At some of the refineries the cathodes of one tank rest directly upon the anodes of the adjoining tank, having been cast with a V wedge on the lugs. This avoids one point of contact and materially lowers cell voltage. The arrangement is known as the Whitehead system or the Baltimore contact.

Figure 69 shows a typical electrolytic tank room or copper refinery.

Fig. 69. Electrolytic copper tank room at Trail. (*Consolidated Mining and Smelting Company of Canada, Ltd.*)

The electrolyte is circulated by means of a centrifugal pump or a Pohle air lift. Two methods are used, one pumping directly in the tanks from the hot wells where the solution is heated by steam to 60°C, the other pumping to an overhead storage tank, then dropping by gravity to the tanks. The latter is the preferred method. Most refineries use an upward circulation, the electrolyte entering the tank at the bottom and being withdrawn at the top. The circulation is consequently in the opposite direction to the settling of the slimes, but the upward velocity is not great enough to reverse the normal downward travel of the slime particles. Some plants are equipped with downward circu-

lation, the solution entering the tank at the top and being withdrawn from the bottom by means of a siphon.

The starting sheet which forms the cathode in the multiple system is made by depositing copper on a blank of rolled copper $\frac{1}{4}$ in. thick in what is known as a "stripper tank." The blank is carefully oiled to prevent the deposited copper from sticking fast. The copper is readily stripped from the blank by means of a groove $\frac{1}{4}$ in. from the edge, or a wood frame around the blank. This starting sheet will weigh 7 to 13 lb. It is made slightly larger than the anode to compensate the increased current around the edges of the electrodes which would otherwise cause nodules on the edges of the cathode.

The schedules differ at the various refineries, depending upon the current density employed. No refinery makes the cathode as heavy as the anode, primarily because of difficulty of inspection and correction, and because of the weakness of the lugs. Most plants make two liftings of cathodes to one of anodes. As a rule the slime is cleaned from the tanks and the anodes only when the scrap anodes are lifted from the tanks. When, however, the anodes have a high silver or gold value, or when they are less pure than normally as the result of considerable amounts of base metals, slime cleaning of the anodes in the tanks occurs more frequently.

The amount of scrap is 10 to 16 per cent in weight of the original copper. It is returned to the blister furnace and recast into anodes.

The refineries employ glue as a colloidal addition agent, adding it to the electrolyte in small amounts daily, more being added to the stripper sections than to the commercial tanks. Glue materially improves the character of the cathode deposit. However, it considerably increases the cathode potential and must be used sparingly. Emulsified mineral oils and by-product sulfonates are also used. Salt is added to precipitate any silver, bismuth, and antimony which may be in solution. Excess of chlorides causes a deposition of $CuCl$ on the cathodes which is lost during the melting process. Usually the electrolyte is kept at 0.02 to 0.03 g per liter of chlorine.

Anode Impurities. Copper anodes contain base metal impurities sometimes alloyed with the silver as well as the copper. The higher the grade of anode, the easier and cheaper the cost of

refining. The usual run of anodes will contain over 99 per cent of copper plus silver. With lower grades of anodes the electrolyte quickly becomes foul, the quantity of slime formed is excessive, and the percentage of anode scrap high. Theoretically, with the low voltage of refining, the more noble or the more electropositive metals than copper should drop to the bottom of the tank as a slime, while the more electronegative or less noble metals should dissolve and foul the electrolyte. However, the problem is complicated by the fact that some of the impurities may be alloyed with copper or silver and will go in the slime as such, also by the fact that some of the soluble impurities will be precipitated either partially or completely by some of the ingredients of the electrolyte.

In practice, the refineries have eight major impurities to take care of, *viz.*, Au, Ag, Se, Te, As, Sb, Pb, and Ni. Selenium and tellurium are combined in the anodes primarily with silver and will go in the slime as selenide and telluride of silver. Any excess of selenium and tellurium is combined with copper and will increase the normal copper content of the slime by the introduction of copper selenide and copper telluride. Lead dissolves at the anode and is at once precipitated completely as $PbSO_4$. Arsenic dissolves at the anode as arsenic acid and as such will go into the electrolyte. Antimony will dissolve as H_3SbO_3 and react with the arsenic acid to produce a basic antimonous arsenate compound which forms a precipitated slime known as "float" slime. This slime is considerably lighter than the silver slime, settles with difficulty, and has a tendency to crust in the wells and to plug up the solution lines. Arsenic will therefore partly go in the slime, the percentage depending upon the antimony content of the anode.

Antimony will saturate the electrolyte and will go in the slime either as basic arsenate, as noted above, or as a basic chloride. Unless an excess of nickel be present in the anodes, practically all the nickel will be found in the electrolyte. Traces of other metals are to be found in the anodes, such as Zn, Co, Fe, Bi, Sn, etc., but usually in such small amounts that they do not influence the refinery practice. Any sulfur in the anode will go into the slime as copper sulfide. Converter anodes—*i.e.*, anodes cast direct from a converter without going through a refining process in reverberatory furnaces—carry an appreciable quantity of

Table 38.   Electrolytic Refining of Copper

	American Smelting & Refining Co., Barber, N.J.	American Smelting & Refining Co., Baltimore, Md.	American Smelting & Refining Co., Tacoma, Wash.	Anaconda Copper Mining Co., Great Falls, Mont.	Canadian Copper Refiners, Ltd., Montreal East, Que.
Electrolyte:					
Sp gr.	1.275	1.265	1.25	1.277	1.25
Percentage Cu	3.5 (44.6 g/l)	3.5 (44.3 g/l)	3.5 (43.75 g/l)	3.55 (45.3 g/l)	3.32 (41.5 g/l)
Percentage free H_2SO_4	16.5 (210.4 g/l)	15.8 (199.87 g/l)	17.0 (212.50 g/l)	13.7 (175 g/l)	16.54 (206.75 g/l)
Temperature, °C	60	60	55	66 inlet, 57 outlet	62
Circulation, gal/min	3.5–5.0	5.0	5.0	6	4.5
Circulation apparatus	Horizontal centrifugal pumps	Vertical centrifugal pumps	Vertical and horizontal centrifugal pumps	Air lifts	Horizontal centrifugal pumps
Current:					
Amp/sq ft cathode	19	18	12–19	21.4	19.16
Voltage per tank	0.16–0.24	0.235	0.22 (17.5 amp)	0.36	0.250
Kw, voltage, and current of generators	1,375 kw	1,250 kw	3-300 kw, 150 volts, 2,000 amp; 2-750 kw, 150 volts, 5,000 amp; 4-1,100 kw, 185 volts, 6,000 amp	8-600 kw, 200 volts, 3,000 amp	7-675 kw, 135–12 volts, 5,000 amp ➤
Current efficiency, %	92.5	94.0	93.0	90	96.74
Kwhr/ton Cu	192	194	192 (15 amp); 218 (19 amp)	312	216
Pounds Cu per kw-day	250	232	250 (15 amp); 220 (19 amp)	154	222
Anodes:					
Composition, % Cu	99.0	99.4	98.0–99.25	99.499	99.4
Length, width, thickness	34½" × 35½" × 1¾"	39½" × 35¾" × 1¾"	37¼" × 27⅞" × 1½"	36½" × 28" × 1½"	36" × 36" × 1¾"
Weight, lb	670	700	530	430	700
Mode of suspension	Cast lugs	Cast lugs	Cast lugs	Cast lugs	Cast lugs
Anode spacing, in	4¼	3⅞	4	3¾	4½
Life, days	28	27	26–34	22	30
Scrap, %	20	18	18	16.0	13.36
Cathodes:					
Size starting sheet, length × width × thickness	37½" × 36½" × 0.028"	41" × 37" × 0.025"	38" × 29" × 0.03"	38" × 29"	37" × 37½" × 0.023"
Weight, lb	10¾–13½	13½	12	7	13 with loop
Mode of suspension	Large central loop	Large central loop	2 small side loops	2 small side loops	Central loop
Replaced after ? days	14	13½	7–17	11	10
Weight, lb	275–295	300	175–225	180	220
Manipulation of electrodes	Overhead cranes	Overhead cranes	Overhead crane	Overhead cranes	Overhead cranes

TABLE 38. ELECTROLYTIC REFINING OF COPPER.—(*Continued*)

	American Smelting & Refining Co., Barber, N.J	American Smelting & Refining Co., Baltimore, Md	American Smelting & Refining Co., Tacoma, Wash.	Anaconda Copper Mining Co., Great Falls, Mont.	Canadian Copper Refiners, Ltd, Montreal East, Que.
Deposition tanks:					
Materials of construction	Wood, lead-lined, concrete, lead-lined	Wood, lead-lined	Wood, lead-lined; concrete, lead-lined	Wood or concrete, lined with 6% antimonial lead	Concrete, lined with 6% antimonial lead
Length × width × depth	Wood: 11'1" × 3'5¾" × 3'9"; Concrete: 11'2" × 3'5½" × 4'	13'5" × 3'7" × 4'1"	8'3" × 2'9" × 3'10'; 12'3" × 2'9" × 3'10"; 14'6" × 2'9" × 3'10"	10'3" × 2'20" × 3'9'	16'7" × 3'7½" × 4'1½"
No. of anodes, cathodes	30, 30	41, 40	22, 23 35, 36 42, 43	32, 33	42, 43
Electric connection	Special single contact	Special single contact	Whitehead single contact	Single contact	Whitehead angle contact
Amp/sq in. cross section	524	400	500	900	375
Anode mud:					
Percentage of anode	1 0	1 0	0 5	0 24	1 0
Au, oz/ton	170-200	200	508	118 532	520
Ag, oz/ton	5,000-10,000	3,000	8,870	11,107 177	4,439 27
Cu, %	22 0	25 0	1 5 untreated, 13'	2 593	34 42
Pb, %	8 5	7 75	11 4	6 0	
Sb, %				6 7	
S, %				2 2	
Se, %				4 9	
Te, %				10 6	20 66
Fe, %				0 19	4 82
As, %				3 8	
Ni, %				0 10	
SiO₂, %				4.0 insoluble	
SO₄, %					
Removed after ? days	28	27	26-34		30

TABLE 38.   ELECTROLYTIC REFINING OF COPPER.—*(Continued)*

	International Nickel Co. of Canada Ltd., Copper Refining Division, Copper Cliff, Ont.	Mt. Lyell Mining & Railway Co. Ltd., Queenstown, Tasmania	Norddeutsche Affinerie, Hamburg, Germany	Phelps Dodge Refining Corp., El Paso, Tex.	Phelps Dodge Refining Corp., Laurel Hill, N.Y.
Electrolyte:					
Sp gr	1 280	1 20	1 25	1 27	1 24
Percentage Cu	3.05 (39 g/l)	3.3 (40 g/l)	2.8 (35 g/l)	3.25 (41.27 g/l)	2.80 (34.72 g/l)
Percentage free H_2SO_4	16.10 (206 g/l)	10.0–12.5 (120–150 g/l)	13.2 (165 g/l)	16–17 (203.2–215.9 g/l)	18.00 (223.2 g/l)
Temperature, °C	65	45–55	55	61	50
Circulation, gal/min	2 5–3	5	4 4	3 5–4	3 75
Circulation apparatus	Vertical centrifugal pumps	Centrifugal pumps		Head tanks	Gravity
Current:					
Amp/sq ft cathode	15 6	20–30	15	20 4	13–26
Voltage per tank	0 229	0 3–0 8	0 25		
Kw, voltage, and current of generators	3–960 kw, 80–160 volts, 6,000 amp	4,315 kw, 90 volts, 3,500 amp	6,800 amp	3–1,500 kw, 143 volts, 10,500 amp; 2–2,250 kw, 143 volts, 15,750 amp	
Current efficiency, %	97 3	92	92–94	85	70–73
Kwhr/ton Cu	190	400		160	148
Pounds Cu per kw-day	254	120		300	325
Anodes:					
Composition, % Cu	99.17	99.21	98 8	99 60	99 2–99 6
Length, width, thickness	36" × 36" × 1⅜"	36¾" × 27½" × 2¼" – 2¾"	35" × 26" × 1⅜"	36" × 36"	56" × 12" × 9⁄16"
Weight, lb	580	560	353	700	110
Mode of suspension	Cast lugs	Copper wire loops cast in corners		Cast lugs	Punched lugs
Anode spacing, in	3½	5½	26	4	11³⁄₁₆
Life, days	28	19–25	15	28	20–27
Scrap, %	12 6	13		13 5	10–14
Cathodes:					
Size starting sheet, length × width × thickness	37" × 38" × 0.026"	38" × 30" × ⅓₂"	35⅝" × 28" × 0.02"	37" × 37" × ³⁄₃₂"	Series system: deposit on anode
Weight, lb	12	8	7.5 with lugs		
Mode of suspension	2 small loops	2 small side loops		Central loop	Series system: deposit on next anode
Replaced after ? days	13 7	3–6	13		94–99
Weight, lb.	260	90–120	143–154		94–99
Manipulation of electrodes	Overhead cranes	Chain blocks and overhead crane		Overhead cranes	Overhead cranes

TABLE 38. ELECTROLYTIC REFINING OF COPPER.—*(Continued)*

	International Nickel Co. of Canada Ltd., Copper Refining Division, Copper Cliff, Ont.	Mt. Lyell Mining & Railway Co., Ltd., Queenstown, Tasmania	Norddeutsche Affinerie, Hamburg, Germany	Phelps Dodge Refining Corp., El Paso, Tex.	Phelps Dodge Refining Corp., Laurel Hill, N.Y.
Deposition tanks:					
Materials of construction...	Concrete, lined with 6% antimonial lead	Concrete, lined with 6% antimonial lead	. . . .	Concrete	Wood or concrete, asphalt lined
Length × width × depth	11'3" × 3'6" × 3'9½" 38, 39	10'3" × 2'9" × 3'9" 21, 22	10'6" × 27½" × 4'33⁄16" 33, 34	13'2" × 3'6½" × 3'9" 33, 34	16' × 5'4" × 5'2"
No. of anodes, cathodes					102 cells of 5 anodes each in series per tank
Electric connection......	Walker	Single contact		Baltimore groove single contact	Busbars form first and last suspension bar each cell
Amp/sq in. cross section	515	500–850	645	400	
Anode mud:					
Percentage of anode..	0.46				0 25
Au, oz/ton..		0 8	0 89	200	100
Ag, oz/ton		66	8,	9,000	2,000
Cu, %	26 93	373	3,650	20 0	30 0
Pb, %	2 09	73	16 5	10 0	9 75
Sb, %	0 20	0 9	4 ?	2 0	4 0
S, %	7 00	0 4	0 0		
Se, %	14 50	9		} 12.5 Se and Te	8 0
Te, %	1 68	3		}	1 0
Fe, %	0 19	0 6			
As, %	0 33	0 2		0 5	1 25
Ni, %	10 76	0 08			
SiO₂, %	0 63	0 02		4 5	17 0
SO₄, %	8 55				
Removed after ? days	28	18–25	28		

TABLE 38. ELECTROLYTIC REFINING OF COPPER.—(*Continued*)

	Raritan Copper Works, Perth Amboy, N.J.	Rhodesia Copper Refineries, Ltd., Nkana, Northern Rhodesia	Société Générale Métallurgique de Hoboken, Belgium	U.S. Metals Refining Company, Carteret, N.J.	Zinnwerke Wilhelmsburg, Wilhelmsburg am Elbe, Germany
Electrolyte:					
Sp gr	1 28	1 210	1 285	1 22	
Percentage Cu	3.75 (48 g/l)	3.7 (45 g/l)	3.5 (45 g/l)	3.2 (39.04 g/l)	35–40 g/l
Percentage free H_2SO_4	17.0 (215 g/l)	9.9 (120 g/l)	17.5 (225 g/l)	16 (195.20 g/l)	150–170 g/l
Temperature, °C	60	65	3 8	55	56
Circulation, gal/min.	4	6 (5 Imperial gal)		3	
Circulation apparatus	Vertical or horizontal centrifugal pumps	Horizontal centrifugal pumps	Vertical centrifugal pumps	Worthite centrifugal pumps	Horizontal centrifugal pumps
Current:					
Amp/sq ft cathode	18	15	14 5	15 4	15.8
Voltage per tank	0 25	0 230	0 18	0 20	
Kw, voltage, and current of generators	2–720 kw, 180 volts, 8,200 amp	800 kw. 5–100 volts, 10,000 amp	1,837 kw, 175 volts, 10,500 amp	2–1,400 kw 3–1,050 kw 1–1,220 kw	10,000 amp
Current efficiency %	92–95	90	92–95	90	94
Kwhr/ton Cu	222	180	150	180	
Pounds Cu per kw-day	216	266	320	260	
Anodes:					
Composition, % Cu	99 50	99 75	99	98 90–99 20	
Length, width, thickness	37" × 28½" × 1½"	37" × 36" × 1¼"	35½" × 35½" × 1½"	36" × 36" × 1¼"	
Weight, lb	490	550	605	525	550
Mode of suspension	Cast lugs	Cast lugs	Cast lugs	Cast lugs	
Anode spacing, in	4	4½	. . . . .	3½	
Life, days	26	30	30	23	29
Scrap, %	13	20	12	15	
Cathodes:					
Size, starting sheet, length × width × thickness	38½" × 30¼" × 0.023"	37½" × 37½" × ¹⁄₁₆"	37" × 38"	37" × 38"	43" × 33½" × 0.6"
Weight, lb	8½	10	13 2	11	
Mode of suspension	Small side loops	Central loop	2 small loops	24" loops	2 small loops
Replaced after ? days	13	15	15	11½	10 and 9
Weight lb	220	220	270	225	
Manipulation of electrodes	Overhead cranes	Overhead cranes	Overhead cranes	Overhead cranes	

TABLE 56.—ELECTROLYTIC REFINING OF COPPER.—(*Continued*)

	Raritan Copper Works, Perth Amboy, N.J.	Rhodesia Copper Refineries, Ltd., Nkana, Northern Rhodesia	Société Générale Métallurgique de Hoboken, Belgium	U.S. Metals Refining Company, Carteret, N.J.	Zinnwerke Wilhelmsburg, Wilhelmsburg am Elbe, Germany
Deposition tanks: Materials of construction	Concrete, lead-lined	Precast concrete, lined with 6% antimonial lead	Concrete, lined with 6% antimonial lead	Concrete or wood, lined with 6% antimonial lead	
Length × width × depth	10'0" × 2'10" × 4'0"	12'6" × 3'7½" × 3'11½"	11'5⅞" × 3'5⅞₁₆" × 3'8½"	11'0" × 3'6" × 3'8½"	
No. of anodes, cathodes	30, 31	32, 33	34, 35 / 38, 39	37, 38	32, 33
Electric connection	Walker	Walker	Walker	Walker	Walker
Amp/sq in cross section	540	440	520	550	
Anode mud Percentage of anode				0 75-1 25	
Au, oz/ton	0 38	0 14	0 6 n 8	200-400	
Ag, oz/ton	58	13 4	10~	8,000-11,000	
	2,350	1,452	5,000-7,000		
Cu, %	25 5	43 55	2-3	12-15	
Pb, %	12 2	0 91	30	10-15	
Sb, %	4 4	0 06	3 5	4-8	
S, %		6 55	5 5		
Se, %	7 0	12 64	2 5	5-8	
Te, %	4 2	1 06	0 5	2-4	
Fe, %		1 42	0 2		
As, %	4 6	0 29	0 2	2-3	
Ni, %	0 3	0 27	0 3	1-2	
SiO₂, %		6 93	7-10		
SO₄, %			15		
			15		
Removed after ? days	26	100		11½	29

sulfur which may increase the copper content of the slime up to 40 or 50 per cent.

Arsenic and nickel are the only metals which dissolve in the electrolyte in sufficient quantity to make a recovery system necessary. The allowable concentration of these metals in the electrolyte is set by their own solubility, the depletion of the cupric ions, and the effect on the cathode deposit produced by this depletion. The most important impurities are arsenic, antimony, and bismuth because of their bad effects on properties of the refined copper and the ease with which they enter solution
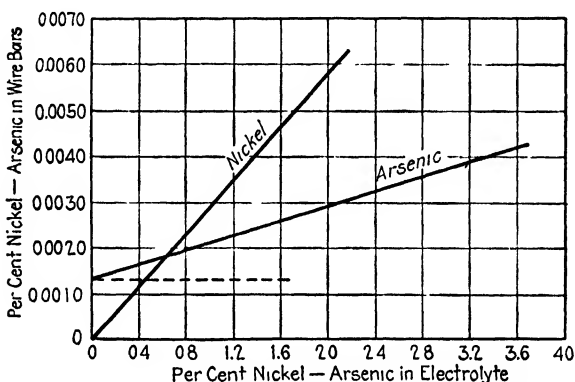
Fig. 70.   Relation of Ni and As in electrolyte to Ni and As content of wirebars made from cathode copper.

and are cathodically precipitated. Bismuth, when present even to the extent of a few thousandths of a per cent, markedly reduces the workability of copper. Arsenic cannot be deposited from H_2SO_4 solutions without simultaneous hydrogen evolution even at exceedingly low current density. The presence of small amounts of soluble chlorides in the electrolyte causes the formation of insoluble oxychlorides of antimony and bismuth which fall into the slime. Arsenic up to about 0.8 per cent in metallic copper improves the rolling properties of copper, but very small amounts of the metal markedly affect its conductivity. As little as 0.0013 per cent As lowers the conductivity by 1 per cent.

The degree of concentration of soluble impurities in the electrolyte has a direct bearing upon the purity of the cathode product, particularly in the case of arsenic and nickel, as shown in Fig. 70.

Purification of Electrolyte. Withdrawals of sufficient electrolyte for purification so that the amount of the chief impurities,

nickel and arsenic, may be controlled are regularly made. The maximum allowable amounts of various impurities depend upon the operating conditions of the individual plant. Various methods for purification of the electrolyte are followed. The simplest one is that in which the copper in the electrolyte is cemented out by scrap iron, but it is now used only as an emergency measure dealing with a bad electrolyte. It makes a foul cement copper which requires retreatment, consumes iron, and wastes both the free and combined acid content of the electrolyte. The next purification method was the manufacture of crystalline $CuSO_4 \cdot 5H_2O$ or bluestone in which the electrolyte was used as a raw material. The process consists of a neutralization of free acid by means of anode copper, the concentration of the neutral liquor by boiling, followed by crystallization and cementation of copper out of the mother liquors by iron

The general method of purification of electrolyte is a cyclic one in which the liquors are sent to insoluble anode tanks at a rate just sufficient to keep the determining impurity at the desired point. Three tanks are operated in cascade, the first producing good cathode copper at about 85 per cent current efficiency, the second producing casting copper or bad copper which is sent to the anode furnaces at about 50 per cent current efficiency, and the third a sludge containing about half copper and half metallic arsenic, from which much of the latter can be eliminated by roasting and sublimation. The liquors, containing only small amounts of copper, are concentrated in evaporators to a point at which all the impurities, except the small amount of arsenic which has escaped the insoluble anode tanks and the sodium and potassium salts, have been precipitated as anhydrous sulfates. This heavy liquor with its suspended solids is then filtered. The bulk of the strong acid is recovered and returned to the electrolyte system. The salts are washed and worked up for nickel sulfate by crystallization.

Metal Distribution in Operation. The effect of impurities may be studied by following one tank of anodes through a typical tank house.

This anode is of very high grade, the copper plus silver content being 99.63 per cent. Usually the furnace charges are carefully made up from the various blister coppers coming to the refinery, in order to obtain anodes of uniform silver content and impurities within allowable limits.

The refined smooth-surface cathode is better than 99.98 per cent Cu, while rough cathodes may run only 99.95. The arsenic has been reduced from a figure above 0.04 per cent to less than 0.001, and the antimony from greater than 0.03 to less than 0.001. Selenium and tellurium, which in the anode were greater than 0.01, have been reduced so that the cathode contains less than 0.0003. In the finished cathode adsorbed gases are the major

TABLE 39. ANALYSIS OF BLISTER COPPER, ANODES, AND CATHODES

Analysis	Blister	Anode	Cathode
Copper....	99 0140%	99 4220%	99.9800%
Oxygen	0.6910%	0.1540%	
Sulfur .	0 0185%	0 0026%	
Arsenic	0 0464%	0 0435%	0 0010%
Antimony	0.0350%	0.0317%	0 0010%
Lead	0.0039%	0 0042%	Nil
Selenium	0 0184%	0.0176%	0 0003%
Tellurium	0 0122%	0 0122%	0.0002%
Nickel	0.0140%	0 0146%	0.0010%
Silver	63.31 oz/ton	62 44 oz/ton	0.30 oz/ton
Gold	0.265 oz/ton	0.265 oz/ton	

LOG OF TANK HOUSE (ONE TANK)

Total weight of anodes..	14,065 lb
Weight of anode scrap...... .	1,678 lb
Weight corroded from anodes ..	12,387 lb
Total electrolysis, 31 days, 17 hr, 55 min	
Weight of deposited copper ..	11,837 lb
Average amp during run .	6,700
Current efficiency, %.	91.3
Slime.................... . .	51 lb 13 oz
Pounds of slime per ton of copper refined....	8.37

Slime analysis:

Copper..	18.80%	
Silver...	51.008%	14,877.73 oz/ton
Gold....	0.2171%	63.32 oz/ton
Arsenic............ ..	3.90%	
Antimony..........	8.04%	
Lead................	1.06%	
Selenium.......... .	4.37%	
Tellurium...........	2.99%	
Nickel....	0.05%	

impurity, accounting for more than half of the 0.02 per cent which is not copper.

Analysis of the weight distribution for a single tank of the anode copper and the slime shows that somewhat less than 40 per cent of the arsenic of the anode is recovered in the slime, all the antimony, all the lead, all the selenium, all the tellurium, practically all the silver, and all the gold, while most of the nickel has passed into the electrolyte. The recovery of the nickel during the purification of the electrolyte and the handling of arsenic along the same lines have been discussed previously. The working up of the slimes will be treated under silver and gold refining.

DISTRIBUTION BY WEIGHTS

(Weights of metallic elements in the anode copper as compared with the weights recovered in the slime)

Distribution	Anode copper	Slime
Total Weight: lb............	12,387	51.8125
Copper.........	12,315	9.74
Arsenic.........	5.35	2.02
Antimony....... ..	3.96	4.16
Lead.........	0.52	0.55
Selenium....	2.18	2.26
Tellurium......	1.51	1.55
Nickel..........................	1.81	0.03
Precious Metals:		
Silver, oz.........................	386.722	385.415
Gold, oz..........................	1.641	1.640

SILVER

The raw material from which pure silver is produced is, in the main, concentrates from anode slimes from copper refining, as well as those of other nonferrous metals such as lead, nickel, and zinc; silver concentrates resulting from the desilverization of lead by the Parkes process; and silver-gold bullion of various compositions including secondary metal and scrap. From copper-refining slimes the crude silver may run 95 per cent Ag, 1 to 3 per cent Au, the remaining 2 per cent being Cu, Bi, Pb, Te, Fe, Ni, Pt, and small amounts of other metals; from the desilverization of lead the crude silver may run 98 per cent Ag, 0.5 per

cent Au, 1.5 per cent Cu, Bi, Pb, and Zn. Such material is cast into anodes and refined electrolytically in a $AgNO_3$-$Cu(NO_3)_2$ electrolyte. Commercial practice may be best portrayed by describing some present-day plants.

Treatment of Copper Anode Mud. In the electrolytic refining of copper, all the precious metals originally in the anodes drop to the bottom of the tanks during the process of electrolysis and
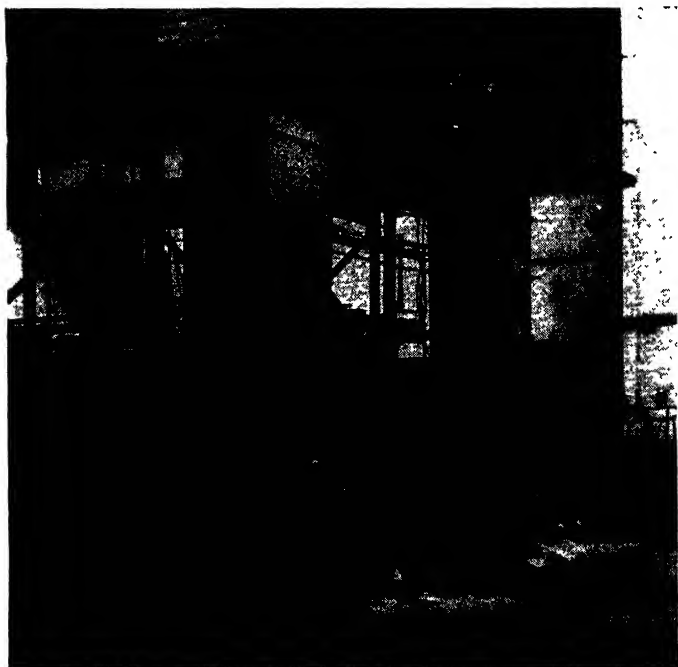
FIG. 71. Doré furnaces. (*Raritan Copper Works.*)

are known as "slime" or "anode mud." When the scrap anodes are lifted from the tanks after 30 days of electrolysis, the slime is sluiced from the bottom of the tank and pumped to the silver refinery. The slime will vary considerably in composition, depending upon the grade of blister copper refined.

On reaching the silver refinery, the slime is allowed to settle in large settling tanks, the liquor being sent back to the tank houses and the slime filtered and washed on an Oliver filter to a cake containing about 35 per cent of moisture. In order to remove the copper, the slime is given a light roast in an oil-fired

oven. This converts all the copper into copper oxide, which is readily leached with 15 per cent H_2SO_4 in agitators, lead-lined iron skeleton tanks with mechanical paddles to keep the slime and solution agitated. The slime, after leaching, contains less than 1 per cent copper and, after again filtering and washing,

RAW SLIME
with solution from electrolytic
copper refinery

Settling tanks
slime settled out, solution overflowing

Settled   Solution returned
slime   to copper refinery

Filter feed tank

Oliver filter
Filtered and washed with water

Slime cake

Filtrate

Roasting furnace
Oxidation at 700 deg. F.

Roasted slime

Raw slime for the
precipitation of
silver from solution

Leaching tanks
Boiled and agitated
with 15 per cent H_2SO_4 solution
and washed with water

CuSO₄ leach
liquor and
wash water

Leached slime

Diaphragm pump

Precipitating
tanks
Solution boiled
in contact with
copper sheets   Filtrate

Filter feed tank

Filtered and washed
with water

CuSO₄   Precipitate
solution

Treated slime
to doré furnaces

FIG. 72.   Flow sheet of slime treatment in silver refinery.

is ready for the fire treatment. This treatment consists of melting and refining the slime in small oil-fired reverberatory furnaces, called "doré furnaces," shown in Fig. 71.

Mosher[10] described the silver refinery of the Raritan Copper Works. The flow sheet of slime treatment is given in Fig. 72.

During the furnace refining process, the lead forms a lead slag which is skimmed off and sent to the lead refinery for further

[10] MOSHER, M. A., *Trans. Am. Inst. Mining Met. Engrs.*, **106**, 427 (1933).

treatment.   Antimony is volatilized and later recovered with the
flue dust.   Selenium and tellurium are partly volatilized, but are
mainly removed by the addition of alkaline fluxes, soda ash, and
niter.   The furnace treatment will take about 40 hr for a charge
of 15,000 lb of wet slime, and will result in about 3,500 lb of
doré metal containing 98.5 per cent Ag, 1.0 per cent Au, with a
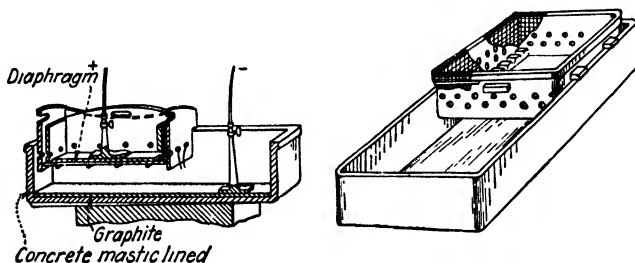
FIG. 73.   Thum cell.
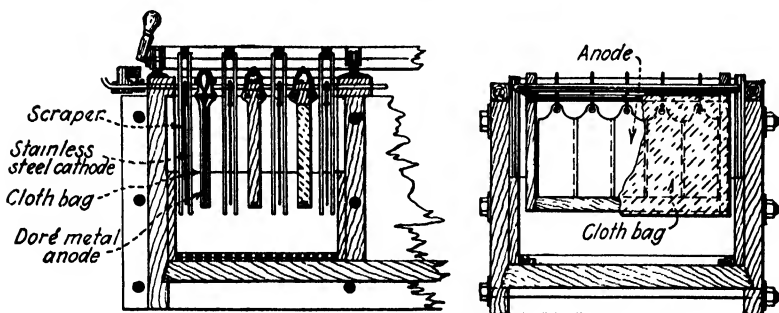
FIG. 74.   Moebius cell.

small amount of metallic impurities.   The doré silver is cast into
anodes and electrolyzed for the parting of the silver from the
gold, using both the Thum and the Moebius systems (Figs.
73 and 74).   The flow sheet for the treatment of the doré anodes
is shown in Fig. 75.[11]

Refining Cells and Their Operation.   In the Thum system the
electrolytic cells consist of shallow, glazed, porcelain tanks, or
mastic-lined concrete tanks, the bottom of which, lined with
graphite slabs, forms the cathode.   The doré silver anodes are
arranged horizontally in wooden frames above the cathode.
These frames are covered with canvas which acts as a diaphragm
and prevents the gold slime from mixing with the cathode deposit.

[11] *Ibid.*

DORÉ (SILVER-GOLD) ANODES

Electrolytic cells–Thum and Moebius
Separation of pure crystal silver from gold and
other constituents of the anode by electrolysis
in silver-copper nitrate solution

Solution storage tank

Dissolving tank
Digestion with nitric acid

Silver nitrate solution   Gold mud

Crystal silver   Gold mud   Anode scrap

Wash cars   Wash cars

Washed with water   Washed with water

Wash water   Washed crystal silver   Wash water   Washed mud

Copper to adjust fineness   Retort furnace Melted and cast

Fine silver bars to market

Boiling tank
Boiled with water and dilute H_2SO_4

Treated mud   Treatment liquor

Cementing tank
Boiled in contact with copper sheets

Silver-gold cement, to doré furnace $CuSO_4$ solution to copper refinery

Centrifugal filter

Dewatered mud   Filtrate

Oil-fired kettle
Boiled with 60° Bé, H_2SO_4

Gold sand   Kettle liquor

Filtros filter
Washed with water

Washed sand   Filtrate

Crucible furnace
Melted and cast

Gold anodes

Wohlwill electrolytic gold cells
Deposition of pure gold by electrolysis in gold
chloride-hydrochloric acid solution

Gold cathodes   Pt-Pd Saturated electrolyte   Silver chloride slime   Gold anode scrap

Wash tank
Boiled with water   Washed cathodes   Dissolving tank   Wash tank

Washwater   Washed cathodes   Boiled with aqua regia-nitric acid evaporated off   Washed with water

Crucible furnace
Melted and cast   Washed scrap   Wash water

Cathode bar   Fine gold bar to market   Platinum-palladium recovery   Gold chloride solution   Silver chloride residue, to doré furnace

Mechanical rolls
Bar rolled into cathode sheets

Platinum sponge to market   Palladium sponge to market

Cathode sheets

Fig. 75. Flow sheet of electrolytic parting and refining of precious metals.

The silver is deposited in a loose crystalline form which is scraped from the bottom of the tank at regular intervals. A Thum cell plant is shown in Fig. 76. The electrolyte for both the Thum and Moebius system is a neutral solution of $AgNO_3$ and $Cu(NO_3)_2$ containing about 60 g per liter of silver and 40 g per liter of copper. Clark and Heimrod[12] state that, with the high gold

[12] CLARK, C. W., and HEIMROD, A. A., *Trans. Electrochem. Soc.*, **61,** 77 (1932).

content of the doré anodes met in some refineries, mechanical cleaning of the anodes every· 12 hr may be necessary. Operation at a current density of 25 amp per sq ft and with an electrolyte of 30 g per liter of silver, 20 g per liter of copper, and 7 g per liter of free HNO_3 is preferable under these conditions. In the Moebius system the anodes and cathodes are arranged vertically in much the same manner as in copper refining, the

Fig. 76. Electrolytic silver refinery (Thum cells). (*Raritan Copper Works.*)

anodes being inclosed in canvas bags in order to retain the gold slime. The cathodes are sheets of stainless steel. Mechanically operated wooden scrapers are used to knock off the silver crystals from the cathodes into trays which are periodically withdrawn and emptied. The current density is approximately 40 to 60 amp per sq ft of anode surface, while cathode current densities are of the order of 26 to 35 amp per sq ft. The cathode deposit of silver crystals is very pure, often 999.9 fine. After washing, it is melted in large graphite retorts and cast into 1,000-oz bars, assaying over 999 in fineness, for the market.

Typical operating data of plants in the United States are given in Table 40. Clark and Schloen,[13] as well as Schloen and

[13] CLARK, C. W., and SCHLOEN, J. H., *Am. Inst. Mining Met. Engrs.*, *Tech. Pub.* 982; *Metals Tech.* 5 (No. 7), October, 1938.

TABLE 40. ELECTROLYTIC REFINING OF SILVER

	American Smelting & Refining Co., Barber, N.J.	Canadian Copper Refiners, Ltd., Montreal East, Que.	International Nickel Company of Canada, Ltd., Copper Cliff, Ont.	Raritan Copper Works, Perth Amboy, N.J.	U.S. Metals Refining Co., Carteret, N.J.
Type of cell	Moebius	Moebius	Thum	Thum	Balbach Thum
Electrolyte:					
Ag g/l	30-50	100	60-70	60	30
Cu g/l	30-45	15	1-5	40	80
Free HNO₃, g/l	0	2	1-3	0	Trace
Circulation	Mechanical scrapers	Stirring by mechanical scrapers	Gravity	Gravity	By convection
Current:					
Amp/sq ft	44 anode / 44 cathode	44 anode / 30 cathode	58	50	60 anode / 40 cathode
Voltage per tank	2 3-2 8	2 8	5 4	1 3	4 0
Current per cell, amp	400-490	500	175	150	200
Current efficiency, %		93	93	98+	95
Kwhr/troy lb Ag	0 298	0 276	0 60	0 33	0 360
Anodes:					
Composition	993-908 parts Ag, 1-90 parts Au per 1,000	903 Ag, 92 Au, 5 Cu parts per 1,000	935 parts Ag, and Au, Pt, Pd	970-990 parts Ag + Au	10-30 parts Au, 10 parts Cu, balance Ag
Length × width × thickness	11½" × 4¼" × ¾"	9" × 6" × ½"	16" × 9" × ½"	19¼" × 21½" × 1 2"	17" × 7½" × ½"
Weight, troy oz	200	150	240	510 (45 lb)	250
Number per cell	16	15	5	1	5 more added as required
Scrap, %	20	25		None	None
Anode basket, length × width × depth	21¾" × 13¼" × 17¾"	21¼" × 15¾" × 2"	29½" × 20½" × 5½"	24" × 21" × 5"	
Life, hr	48	28-34	72	36	Worked to completion
Cathodes:					
Material	Stainless steel	Rolled silver sheets	Graphite and carbon	Graphite and carbon	Graphite and carbon plate
Length × width × thickness	19¼" × 10½" × ₁/₁₆"	12" × 20" × ₁/₁₆"		24" × 21" × 5"	24" × 52" × ½" (cover cell bottom)
Number per cell	5	6		1	
Cells:					
Number	180	15	40	147	306
Length × width × depth	27" × 25" × 26"	30⅛" × 30⅞" × 24⁹/₁₆"	52" × 24" × 9"	48" × 24" × 7"	24" × 52" × 9"
Material of construction	Haveg	Steel, rubber, and brick lined	Concrete, asbestos, mastic-lined	Concrete, asphalt-lined	Concrete, lined with Harvel
Cell arrangement	Series	3 sets of 5 in series	Series	Series	40 or 50 in series per circuit
Ag removed after ? hr	24	12	8	12	Every 4 hr
Anode Slimes:					
Per cent	0-15	15	8	3	4-6

Elkin,[14] have described the recovery of precious metals and selenium and tellurium production at the Montreal East plant of the Canadian Copper Refiners, Ltd.

The gold slime resulting from the silver electrolytes contains all the gold, platinum, and palladium which was originally present in the blister copper. It is treated with H_2SO_4 to remove the excess of silver present and is then melted in graphite crucibles and cast into gold anodes to be electrolyzed using the Wohlwill process.

Colcord[15] has described the parting plant of the U. S. S. Lead Refinery, Inc., at East Chicago, Ind., where doré metal, the product of cyaniding silver and gold ores and of refining lead bullion and copper bullion, is treated. Doré metal contains 95 to 98 per cent Ag, 1 to 5 per cent Au, the balance being mostly copper with small amounts of Pb, Te, Se, and Bi. Modified Thum cells are used with an $AgNO_3$-$Cu(NO_3)_2$ electrolyte running 50 to 55 g of silver per liter and 60 to 75 g of copper with traces of free HNO_3. Horizontal graphite plates are used as cathodes, and the doré anodes are placed horizontally in a basket partly immersed in the electrolyte. The basket has a bottom of cotton duck and rests in a basket holder supported from the longitudinal sides of the cell. The silver is deposited in crystalline form. It is periodically scraped from the cathode and removed from the cell by aluminum shovels having perforated bottoms to allow the escape of the electrolyte. The crystals are washed free of electrolyte, allowed to drain, dried, and melted into bar silver. The gold and insoluble impurities are left behind in the basket.

GOLD

The electrolytic process employed for gold refining is due to Wohlwill. It was first used at the Norddeutsche Affinerie, Hamburg, in 1878, and since that time has found almost universal adoption. In connection with copper refining it is employed for the recovery of gold from the anode residues from the silver cells, from which the excess of silver has been removed by parting with H_2SO_4. The anodes contain platinum and palladium. The Wohlwill process, which is used for the refining of gold in all

[14] SCHLOEN, J. H., and ELKIN, E. M., *Trans. Can. Inst. Mining Met.*, **49**, 143–190 (1946); *Can. Mining Met. Bull.* 408.

[15] COLCORD, F. F., *Trans. Am. Electrochem. Soc.*, **49**, 351 (1926).

the United States mints, consists in electrolyzing gold anodes in a hot acid solution of gold chloride. The solution, which is kept at approximately 70°C, contains 7 to 8 per cent of gold and 10 per cent HCl, the density being 1.30. In order to keep down the interest charges on the gold tie-up, a high current density of 110 amp per sq ft (11.8 amp per dm^2) of cathode surface is used. This necessitates a thorough stirring of the electrolyte, which is accomplished by means of a small air lift. The cathodes consist of thin ribbons of rolled gold. The deposit which adheres firmly to the cathodes is exceedingly pure, averaging 999.75 gold fineness. After thorough washing, it is melted in a graphite crucible and cast into standard bars for shipment.

Anode Impurities. In copper and silver electrolysis, the more noble metals have been insoluble and have formed the slime. In gold electrolysis, however, the platinum and palladium are totally soluble and are allowed to accumulate in the electrolyte until present in sufficient quantity to recover. Chemical methods, following the ordinary quantitative analytical separation of these metals, are used in the process of recovery, depending upon the precipitation of both metals, when in an oxidized condition, by NH_4Cl to separate them from the bulk of the gold in the electrolyte.

The amount of platinum and palladium recovered is small; yet owing to the large tonnage of copper refined, the high prices of these metals, and the efficiency of the process, the recovery is commercially successful.

Current Density and Cell Operation. The rate of operation is of great importance in gold refining, owing to the high interest charges of the metal tied up. This is essentially the reason for the very high current density employed.

The électrolysis tanks are of glazed porcelain or chemical stoneware. They are relatively small in size, since the electrolyte is an expensive one. The cathodes, having the same area as the anodes, are of thin rolled gold sheet. In copper refineries the anodes are fairly thin. In governmental refineries or mints where interest on metal tied up is not a factor, the anodes may be fairly thick. They are generally suspended in the bath by means of gold or silver hooks.

In a typical case in a mint, the anodes may contain 94 per cent Au, 5 per cent Ag, and 1 per cent Cu, Pb, Pt, Pd, with traces of

other platinum metals. Of these metals, Au, Cu, Pb, Pt, and Pd dissolve anodically; silver and the other platinum metals (Ir, Rh, Ru) remain chiefly in the slime, the former as AgCl. Copper may accumulate in the electrolyte to a considerable extent without the danger of cathodic deposition. Lead can be kept at a low concentration by the addition of H_2SO_4. Generally the time of regeneration of the solution is set by the accumulation of the platinum and palladium. In their pure state platinum and palladium, as a result of passivity, act almost like insoluble anodes in chloride solutions. They dissolve readily, however, when alloyed with gold. At periodic intervals, due to the accumulation of impurities, part of the electrolyte is drawn off for purification and replaced by a strong $AuCl_3$ solution.

A high current density is necessary to consume the anodes rapidly and hurry the gold through the process. It is desirable, however, that the electrolyte contain a minimum of the expensive gold salt. A balance must be struck between these factors, in that a high current density requires a high gold electrolyte to allow the production of a coherent cathode deposit. Increase of temperature gives improved deposits for any given current density, although high temperatures tend to increase the amount of gold in the slimes and cause the loss of HCl by volatilization.

Electrolyte Purification. The electrolyte withdrawn for purification may be freed of gold by the use of SO_2 or $FeSO_4$ and the platinum precipitated by NH_4Cl as $(NH_4)_2PtCl_6$. Palladium may be extracted with ammonia after evaporation to dryness, and copper may be removed by scrap iron. The platinum recovered during the treatment of gold bullion from various sources may amount to 0.07 per cent and palladium to 0.001 per cent of the weight of bullion refined. The slimes contain gold (up to about 15 per cent of that cathodically precipitated), AgCl, $PbSO_4$, and the rarer platinum metals. The $PbSO_4$ is removed by treatment with Na_2CO_3 solution, followed by HNO_3. The AgCl is fused and poured off, while the residues are generally recast into fresh anodes. The AgCl is reduced to the metal, which is then returned to the silver refinery.

In general the platinum and palladium are recovered from the electrolyte when they reach a combined concentration of 50 g per liter. The solution containing these metals is treated with NH_4Cl and HNO_3, which precipitates them as $(NH_4)_2PtCl_6$ and $(NH_4)_2PdCl_6$. These compounds are filtered, dried, and reduced

TABLE 41. ELECTROLYTIC REFINING OF GOLD

	American Smelting & Refining Co., Barber, N.J.	International Nickel Company of Canada, Ltd., Copper Cliff, Ont.	Norddeutsche Affinerie, Hamburg, Germany	Raritan Copper Works, Perth Amboy, N.J.	U.S. Metals Refining Co., Carteret, N.J.
Electrolyte:					
Au, g/l	140 g/l 150-200	100 g/l 90-100	160 g/l 85-110	120	100 g/l 100
Free HCl				10%	
Sp gr.	1.24 at 50°C	1 140			1.14 at 75°C
Temperature, °C	55-65	60	65-70	60	75
Circulation	Air	Air		Air lift	Air agitation
Current:					
Amp/sq ft anode	145	95	67-102	116	100
Voltage per tank	1½	2 0	0 5-0 7	0 70	1
Current per cell, amp	400-500	165	150-230	435	150-180
Current efficiency, %	99+			99+	99+
Anodes:					
Composition	980-994 fine	995 fine	985 fine	965 fine	98% Au, 1% Ag, 0.2-0.5% Pt, 0.2-0.5% Pd
Weight, troy oz.	115-140	70	28 9	145	120
Length × width × thickness	8½" × 4¾" × ⅜"	9" × 3" × ⅜"	4½" × 3⅜" × ¼"	9" × 5" × ⅜"	4½" × 9" × ⅜"
Number per cell	6	6	12	6	4
Scrap, %	10	20		13-14	16-20
Life, hr.	16+	20	.	18-23	20
Cathodes:					
Material	Rolled gold	Rolled gold	Rolled gold	Rolled gold	Rolled gold
Weight, troy oz.	1½	25-50 (final)	0.42 (original)	Starting sheet 1, final 65	1 4
Length × width × thickness	12½" × 3⅞" × 0.003"	12" × 2½" × 0.004"	3⅞" × ⅜" × 0.005	10" × 2¼" × 0.0035"	9" × 3" × 0.005"
Number	8	9	12-23	10	9
Purity	999 75+	999 8+	999 95+	999 75	999 75
Tanks:					
Material	Haveg	Porcelain	Berlin porcelain	Porcelain-ceramic	Coor's porcelain
Length × width × depth	19½" × 12½" × 12½"	10½" × 10½" × 12"	15⅜" × 9⅝" × 7⅞"	20" × 12" × 14"	12" × 12" × 14"
Anode mud:					
Per cent.		5%			5-8%
Composition	Au, 800 to 967 fine Ag, 190 to 30 fine	AgCl + Au	15-40% AgCl, balance Au	AgCl + Au	85-90% Au, balance silver chloride

to metal. They are parted by dissolving the metal in aqua regia, boiling with HCl to drive off excess HNO_3 and reduce the palladium, and adding NH_4Cl. This precipitates the platinum as $(NH_4)_2PtCl_6$ and leaves the reduced palladium in solution. After filtering off the platinum salt, HNO_3 is added to the solution, oxidizing and precipitating the palladium salt. Each is then reduced to sponge metal and marketed.

Typical operating data for gold-refining plants are given in Table 41.

Superimposed Alternating-current Process. For the treatment of anodes of high silver content, Wohlwill modified his process by using a pulsating current in which an alternating current of low frequency and greater current density is superimposed on the electrolytic direct current. The quantities of gold dissolved and deposited are functions only of the direct current, but the use of the alternating current allows the employment of higher current density and permits the electrolysis of anodes comparatively high in silver by causing the adherent film of AgCl to flake off rapidly. There is also a reduction of the amount of gold entering the slime. The alternating current opposes passivity which would otherwise set in in a high silver content anode at the insulating AgCl layer formed over the gold anode, lessening the active area and increasing the effective current densities. In operation, anodes run 80 to 90 per cent gold, greater than 6 per cent silver, and the balance platinum, palladium, and the rare metals; the d.c. current densities are of the order of 120 to 160 amp per sq ft, and the superimposed alternating current 120 to 250 amp per sq ft. The anode mud consists of 1 per cent Au, 95 per cent AgCl, with $PbSO_4$ and a trace of the base metals and the rare metals. The d.c. cell voltage is lower than in the usual method, being from 0.8 to 1.1.

In copper refineries, owing to the removal by H_2SO_4 of the silver remaining with the gold slimes from the silver-refining cells, the modified Wohlwill process employing alternating current is generally not used, but the method does find employment in the government mints and assay offices.

NICKEL

At the present time by far the largest share of the world's nickel production is obtained from the Sudbury nickel field in

the province of Ontario, Can. The ores are copper-nickel sulfides containing cobalt, iron, and precious metals. The ores are smelted to low-grade mattes which are then blown in basic converters for the removal of iron. The product of these con-
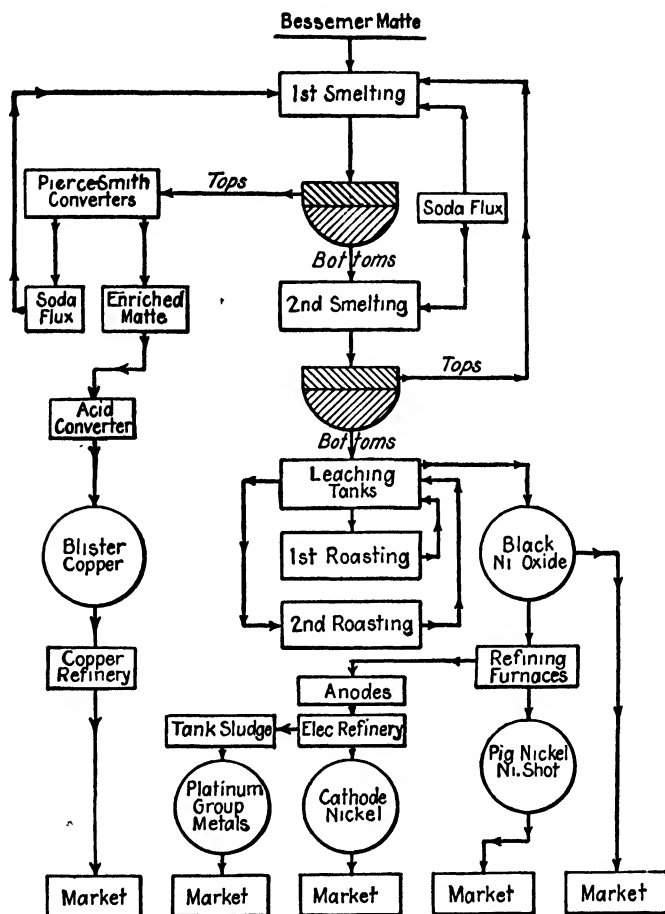
FIG. 77. Flow sheet of the International Nickel Company of Canada, Limited.

verters, termed "bessemer matte," is shipped to the nickel refineries where the process is a combination thermal and electrolytic one. The flow sheet for the process is given in Fig. 77. The discussion will not be concerned with the Mond carbonyl process but only with processes involving electrolytic operations.

The International Nickel Company process was based on the fact that in a molten system containing nickel sulfide, copper sulfide, and sodium sulfide, in general two liquid layers are formed, the upper carrying the bulk of the sodium and copper sulfides and the lower the bulk of the nickel sulfide. A separation was made in these two layers. Peek[16] has described the refining of nickel-copper matte at the Port Colborne plant of the International Nickel Company.

The bessemer matte, containing approximately 54 per cent Ni, 26 per cent Cu, 20 per cent S, and 0.30 per cent Fe, was charged into a standard water-jacketed blast furnace with coke and revert top soda flux from a subsequent operation. The essential reagent was sodium sulfide or sodium sulfate, the latter being reduced by the coke of the charge to the former. On solidification of this first smelting in pots, a top and bottom were formed, effecting a dividing line between the two metals. About 90 per cent of the total copper in the form of top was transferred to Pierce-Smith converters, where it was blown to blister copper ready for market. The separation between top and bottom was marked by a clean line of cleavage.

The bottom, containing the nickel, went to a second smelting with soda flux. From the second smelting the top went back to the first smelting of bessemer matte. The second bottom—nickel sulfide—showed the following analysis: Ni 70 per cent, Cu 0.90 per cent, Fe 0.25 per cent. This was broken up and ground in ball mills. From the ball mill the nickel sulfide went to leaching tanks where the mechanically contained soda was washed out with water and the iron with dilute H_2SO_4. The nickel sulfide was then given one chloridizing roast and leached to remove the copper, and a second roast with soda ash to remove all fractional remaining impurities. The resulting black oxide of nickel of the following analysis: Ni 77.60; Cu 0.10; Fe 0.25; Si 0.10; and S 0.015 per cent, was ready for the market or for reduction to metal in the open-hearth furnace. It was tapped from the furnace into pig nickel, nickel shot, and nickel anodes. The nickel anodes went to the electrolytic refinery.

The Orford process described above served well for many years in the production of the major portion of the world's nickel requirements. A better process has been developed for

[16] PEEK, R. L., *Eng. Mining J.*, **130**, 482 (1930).

the separation of copper, nickel, and platinum metals in matte. This new process subjects the matte to controlled cooling, flotation, and magnetic separation. The matte flotation operations in the new nickel oxide sinter plant commenced in 1949 and reached full-scale production, practically replacing the Orford process. This has been a change of major significance. The sintering operations were transferred from Port Colborne to Copper Cliff, Ontario.

Anodes and Cell Operation. The anodes are rather rough on top but are sufficiently uniform as to thickness. They are removed from the molds and stacked upright, resting on their lower ends. A portable electric grinder then brightens the lower side of the lugs to make good electrical contact on the tank busbars. Anodes are 36 by 27 in. below the lugs and of somewhat irregular thickness, weighing about 425 lb each on an average.

Starting blanks were originally aluminum sheets but were replaced later by stainless steel $38\frac{1}{4}$ by 29 by $\frac{3}{16}$ in., with two tangs each 6 by $5\frac{3}{4}$ in., to the top of which is riveted and soldered the iron crossbar of $\frac{1}{2}$- by $1\frac{3}{4}$-in. section. Side and bottom sticks 1 in. square are applied to these to prevent the starting sheet from covering the edges. Each blank weighs about 30 lb complete.

Starting sheets are provided with two loops $20\frac{1}{2}$ by $2\frac{1}{2}$ in. before bending, made by shearing some of the sheets, attached by Morrow clip machines. The sheets are 36 by 28 in. and weigh about 11 lb each. Cathodes average approximately 128 lb each.

The tanks are of concrete 6 in. thick, with a mastic lining $1\frac{1}{2}$ in. thick, and are built in blocks of two tanks each. Inside the lining they measure 16 ft $9\frac{1}{2}$ in. by 2 ft $10\frac{1}{2}$ in. by 5 ft 2 in. deep. At one end is a $2\frac{1}{2}$-in. overflow pipe, opening at 6 in. above the bottom and terminating in an overflow basin $9\frac{1}{2}$ by 8 by 4 in. deep at the top of the tank. The overflow basin projects 7 in. beyond the outer end of the tank and is provided with a level-regulating wooden dam and a perforated outlet from which the rejected electrolyte drains down into a funnel and is led through a short section of hose to the foul-return launder. Diaphragms are used between anodes and cathodes, being of canvas cloth or a special type of muslin. They are so constructed

and placed in the tank that anode and cathode chambers are formed.

Along the outer side of each tank is a hard-rubber header, connected at its center to a $1\frac{3}{4}$-in. rubber hose riser from the pure solution main. Thirty hard-rubber nipples along the upper surface of the header, each having a $\frac{1}{4}$-in. soft-rubber feed pipe attached, lead pure solution to the cathode boxes. Along the tops of the sides are hardwood top boards 6 by 2 in., notched at their lower part to receive the ends of the wedges that secure the cathode boxes in place. The outer boards also have holes opposite each cathode box through which the rubber feed pipes are led.

There are 30 cathode chambers in each tank. These are made of spruce wood, with sides of heavy canvas calked into a groove along the sides and bottom rail of the box and tacked to the top rails. The legs of the boxes stand upon notched rails fastened against the sides of the tanks and 14 in. above their bottoms. The notches ensure correct spacing of the boxes.

The operating voltage is 2.4 to 2.5 per cell, with 4,800 amp. The temperature is held around 57°C. With 405 sq ft of active cathode area, the current density is approximately 11.5 to 12 amp per sq ft (1.25 to 1.3 amp per dm²). The electrolyte flows into each cathode box at the rate of about 0.7 cu ft per hr; hence the average outward flow velocity through the canvas sides is about 0.05 ft per hr. This flow is swifter than the velocity of copper or iron ions moving under the unit potential fall between the anodes and cathodes, so they are thus excluded from the cathode side of the canvas. Since the cathodes are immersed in a solution nearly free of copper and iron and continually renewed by the flow of pure solution, the metal plated out contains only trifling amounts of these impurities. Nickel ions resulting from the dissolution of anode metal have to travel from the plating cells through the cementation and iron-removal process and return by way of the pure solution flow pipes, tank headers, and solution feed pipes to the cathode boxes before they may be discharged on the cathodes.

The flow pipes and the return flow launders are of wood throughout. There is little current leakage, and a net cathode current efficiency of 95 per cent is held month after month.

Anode slime in part falls to the bottom of the cells, whence it

is removed periodically, and in part adheres to the anode scrap. The scrap is accordingly scrubbed with a stiff broom to loosen the slime, often tightly adherent, which is then washed off with a stream of electrolyte.

Electrolyte. In earlier practice the purified electrolyte contained nickel sulfate equivalent to about 40 g Ni per liter, and about 20 g boric acid. Copper and iron should each be less than 0.005 g per liter. The electrolyte enters the catholyte box at an acidity equivalent to pH 5.2. During refining, the electrolyte decreases in nickel content, leaving the tank at a pH of 4.0. If the cementation method be used, the electrolyte is purified of copper by passage over finely divided nickel made by charcoal reduction of green nickel oxide. Air is blown into the solution to oxidize the iron which is then precipitated as $Fe(OH)_3$. Further removal of iron is obtained by adjusting the pH of the solution to 5.2 and heating it to approximately 57°C, at which point ferric sulfates are precipitated. A suspension of nickel carbonate in water is fed in to neutralize the acid set free by hydrolysis of ferric iron. The electrolyte is then cooled down to 52°C and returned to the cells through rubber-lined or hard-rubber piping. Every precaution is taken to keep the electrolyte out of contact with metals, the liquid coming in contact only with hard rubber, mastic, or wood, and in a single case with lead at the discharge box end of the cell, where there is a lead apron.

Chlorides are not added for anode corrosion but they are present from various sources to the extent of 75 mg per liter. The sulfide content of the anode keeps it depolarized. It is interesting to note that the depolarized plater's anode is made from pure nickel containing a small amount of sulfur. The sulfur content of the electrolytically refined nickel is negligible.

Fedot'ev[17] states that increase of current efficiency is favored by increase in nickel sulfate concentration, decrease of sulfuric acid concentration, increase in cathode current density, and increase in bath temperature. Since the upper limit of pH is 6.5, at which hydrolysis of nickel sulfate begins, in practice a pH of 5.5 is used, at 50 to 60°C and at a fairly wide range of current density. Impurities such as copper and iron that may enter the solution from the anode may deteriorate the nickel deposit. Iron raises the hardness of the deposit and increases

[17] FEDOT'EV, N. P., *J. Applied Chem.* (*U.S.S.R.*), **15**, 5–24 (1942).

strains in it, while iron concentration of 3 to 4 g per liter causes the nickel deposit to crack and peel; copper less than 0.5 per cent in the nickel deposit does not affect the appearance, but at higher concentrations the deposit shows dark spots and spongy growths.   This may occur as a result of faulty diaphragm operation, which permits access of copper from the anolyte.   Zinc at over 0.01 g per liter causes dark spots.   The electrolyte solution must contain a sufficiently high concentration of nickel ions, it must be free of impurities, it must contain chlorides to avoid passive condition of the anodes, and proper pH must be maintained by buffers such as boric acid.   Sodium salts give better nickel deposits than do ammonium salts.

Electrolytic nickel dissolving cells are used for restoring the metal content of the electrolyte.   In contradistinction to copper refining where the metal content increases, the nickel content in this particular method decreases and necessitates the addition of further metal values.

Anode Slimes.   At periodic intervals slimes are drained from the tanks through an opening ordinarily kept closed by a lead plug in the center of the bottom.   Slimes go to settling and washing tanks on the floor below and then to filters, from which they are removed for precious metal recovery.

The filter cake is calcined and its sulfur content reduced to about 0.2 per cent, after which it is smelted with coal in open-hearth furnaces and cast in regular anode molds to form secondary or precious metal anodes.   These are electrolyzed in special sets of refining tanks.   To prevent loss of the very high-grade slime from these anodes, they are wrapped in closely woven cotton duck.   The anode scrap is carried to the precious metal slime-concentrating plant where the slime is carefully removed from the scrap.   The latter is then returned to the precious metal anode furnace.   Precious metal anodes contain approximately 24 per cent Cu and 73 per cent Ni.   Secondary slime contains about 2 per cent of the platinum group metals and is concentrated by acid treatment to a product containing 40 to 50 per cent platinum group metals.   This is soldered up in steel cans and shipped to the platinum refinery in Acton, London, England.

In starting a new installation, considerable quantities of H_2O_2 are added during the first three days to get rid of organic matter in the bath, the organic matter arising from various sources including the wooden side boards or "restrainers."

Cathodes. Cathode nickel is not remelted. On removal from the refining tanks the cathodes are washed and soaked overnight in warm water to ensure removal of nickel salts. They are then cut into squares either 2, 4, 6, 8, or 9 in., as specified by the customer, and packed in barrels for shipment.

Operating data on nickel refining are summed up in Table 42.

TABLE 42. ELECTROLYTIC REFINING OF NICKEL

	Sulfate electrolyte	Sulfate-chloride electrolyte
Electrolyte:		
Ni, g/l..........	40	50–60
Boric acid, g/l...........	20	20
Sodium sulfate, g/l. ...	35	
Sodium chloride, g/l. . .		50
Temperature, °C .	52–57	52–57
Circulation apparatus. .	Hard-rubber pumps	Hard-rubber pumps
Current:	10 rotaries, each 1,100 kva	10 rotaries, each 1,100 kva
Amp per tank..	5,000–5,500	6,500
Voltage per tank.......	2 4	2 4
Current efficiency %...	98	98
Kwhr/lb Ni	1 1	1 1
Anodes:		
Composition...	95% Ni, 2.5% Cu, 0.75% Fe, 0.75% S, precious metals, ¾ oz/ton	95% Ni, 2.5% Cu, 0.75% Fe, 0.75% S, precious metals, ¾ oz/ton
Length, width, thickness.	36″ × 27″ × 2″	36″ × 27″ × 2″
Weight, lb . .	490	490
Mode of suspension. .	Cast lugs	Cast lugs
Life, days	32–33	30–32
Scrap, %	36–40	35
Cathodes:		
Starting sheet blanks	Stainless steel	Stainless steel
Starting sheet, length × width	36″ × 28″	36″ × 28″
C.d., amp/sq ft	12	15
Weight, lb...	11–12	11–12
Mode of suspension. ...	Nickel loops	Nickel loops
Replaced after ? days....	14	12–14
Weight, lb.	135	135
Deposition vats:		
Length, width, depth....	16′9½″ × 2′10½″ × 5′2″	16′9½″ × 2′10½″ × 5′2″
Number of anodes, cathodes..............	31, 30	31, 30
Tank material..........	Reinforced concrete, mastic-lined	Reinforced concrete, mastic-lined
Anode mud:		
Composition:		
From primary anodes.	Precious metals 12 oz/ton, Ni 15–20%	Precious metals 12 oz/ton, Ni 15–20%
From secondary anodes.	Precious metals 500 oz/ton	Precious metals 500 oz/ton

Hybinette Process of Nickel Refining. An electrolytic nickel extraction process devised by Hybinette found employment at Kristiansand, Norway. The process was employed by the British-American Nickel Corporation at its refinery at Deschenes, Que. A bessemer matte running Ni 53, Cu 28, S 18, and Fe 0.25 per cent was granulated and, after screening through 10 mesh, was charged into cementation tanks, through which flowed the foul electrolyte from the nickel deposition tanks. Inasmuch as the bessemer matte was semimetallic, the metallic portion cemented out the copper in the electrolyte, while an equivalent amount of nickel went into solution. The metal transfer was facilitated by operation at about 21°C. The resulting copper-free electrolyte and the foul solution from the deposition tanks flowed in opposite directions through a heat interchanger to preheat the foul liquor.

The spent matte from the cementation tanks (now having 44 per cent Cu and 38 per cent Ni, the copper having been increased and the nickel reduced) was excavated and sent to eight-hearth Wedge roasters and roasted to about 1 per cent sulfur. The hot calcines were screened, oversize being returned to the roasters and the fines discharged into a leaching launder and conveyed to leaching tanks of about 90-ton capacity. The leaching solution was depleted electrolyte from the copper deposition tanks (copper 30 g per liter and H_2SO_4 80 g per liter). The copper-enriched solution (copper 50 g per liter, H_2SO_4 50 g per liter) passed through clarifying cones, then through a series of three-tank cascade electrodeposition vats. These were lead lined and contained eight cathodes and nine insoluble lead anodes. The overflow from the last tank returned as leach liquor.

Some nickel was dissolved with the copper and accumulated in the copper electrolyte. A portion of the spent electrolyte was continuously removed and sent to complete depositing-out tanks, where all the copper was removed. The resulting liquor was worked up for nickel salts.

The nickel electrolyte was also continually enriched with nickel in the cementation tanks, where the copper cemented on the matte was replaced by an equivalent amount of nickel. It was necessary, therefore, continually to withdraw portions of the solution which were evaporated and crystallized as above. The leached, roasted matte was excavated, mixed with coke breeze

and limestone, and melted in a three-phase resistance furnace. The metal was tapped intermittently into a brick-lined ladle and poured into cast-iron anode molds (24 by 36 in.). Anodes contained about 68 per cent Ni, 26 per cent Cu, and 0.40 per cent Fe.

The anodes were encased in bags to catch slimes and suspended in lead-lined tanks carrying 36 anodes and 35 cathodes. Cathodes consisted of iron or copper plates (24 by 36 in.) suspended in "Hybinette bags," consisting of wooden frames with canvas sides, acting as diaphragms.

Copper-free nickel electrolyte from cementation tanks previously described was fed to cathode bags through rubber tubes from a lead header at a rate sufficient to maintain a head of about 1 in. over the level in the anode compartment. This was to prevent anolyte containing copper from flowing into the cathode bags and contaminating the nickel. The iron or copper cathodes were painted with graphite to facilitate stripping. Nickel sheets weighing about 30 lb were stripped from cathodes about every 10 days, washed with dilute H_2SO_4, and cut into small squares for shipment; or they were melted in electric furnaces and cast into ingots.

Electrolytic nickel analyzed approximately: Ni 98.25, Co 0.75, Cu 0.03, Fe 0.50, C 0.10, Pb 0.20 per cent.

Anode scrap was remelted and cast into molds. Slag from the melting furnace was shipped back to the smelter for retreatment. Slimes from the anode tanks were treated for the recovery of precious metals.

Falconbridge Nikkelverk, Aktieselskap, practice smelts the nickel-copper ore to a high metal matte, which is crushed, ground, and roasted to remove most of the sulfur. The roasted ground matte is leached with an acid solution to remove copper. The filtrate goes to a copper electrowinning plant using insoluble anodes. The filter cake containing nickel is washed, dried, and melted with coke to form crude nickel anodes.

Falconbridge Nikkelverk practice at Kristiansand, Norway, is similar in many respects to that of the International Nickel Company in the nickel refinery. Anodes run as high as 16 per cent Cu, with less than 1 per cent each of sulfur and iron. Tank amperages are 5,000 at voltages of the order of 2.4. Anodes and cathodes are slightly smaller. These are not removed in groups

mechanically but individually by hand so that anode scrap is about 22 to 23 per cent. Tanks are of concrete, painted with asphalt-gilsonite mixtures. Practice tends toward chloride electrolytes and away from those containing only sulfates so that cobalt separation may be practiced.

Malleable nickel sheets suitable for cutting by dies and stamping into coinage[18] are made in the refining cell to controlled thickness by the insertion of ceramic pipes which continuously circulate electrolyte across the face of the cathodes, thus eliminating inclusions, products of hydrolysis, striations, or surface nodules or unevenness.

LEAD

With one exception, attempts to refine lead electrolytically have seemingly failed or have progressed no further than the laboratory experimental stage. The successful electrolytic method, known as the Betts process,[19] is used in the large refineries at Trail, B.C., East Chicago, Ind., Omaha, Neb., Oroya, Peru, Newcastle upon Tyne, England, as well as at some continental European plants.

In this process anodes of lead bullion and cathodes of electrolytic lead in sheet form are connected in multiple as in the electrolytic refining of copper. They are supported on copper bars across a tank containing lead fluosilicate ($PbSiF_6$) and free hydrofluosilicic acid (H_2SiF_6) as electrolyte. During electrolysis a slime or anode mud is formed (on the anode) which contains practically all the impurities. It is collected from the anode and from the bottom of the tank and treated for the recovery of Sb, As, Bi, Cu, Ag, Au, Pd, Se, and Te. The lead deposit on the cathode is melted together with the starting sheet and cast into bars.

As a result of electrolysis, Pb, Sn, Zn, Fe, Ni, and Co go into solution while Cu, Sb, As, Bi, Cd, Ag, Au, Se, and Te remain at the anode. In the first group tin will invariably deposit with the lead, since these two metals are so close together in the electrolytic series. It is therefore necessary to subject the lead bullion to a softening treatment before it is cast into anodes. The other soluble metals will not precipitate with the lead. Of

[18] Private communication from A. M. Grönningsaeter.
[19] BETTS, A. G., U.S. Patents 713,277 and 713,278 (Oct. 9, 1902); 891,395 and 891,396 (June 23, 1908); 918,647 (Apr. 20, 1909).

the insoluble metals small amounts of antimony may pass to the cathode, especially when a current density as high as 17 to 18 amp per sq ft (1.8 to 1.9 amp per dm^2) and a temperature of 37 to 38°C are employed. This may be removed by poling the cathode lead with air in a kettle, which at the same time will separate any tin that may be present.

Electrolyte. In making the electrolyte at the plant, H_2SiF_6 is formed by the action of HF on SiO_2 and then allowed to combine with lead, PbO, or white lead to yield $PbSiF_6$. Commercial hydrofluoric acid containing 33 per cent HF may be used, or it may be produced at the plant by the action of H_2SO_4 on fluorspar according to the following equation:

$$CaF_2 + H_2SO_4 = 2HF + CaSO_4$$
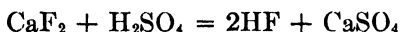
In practice, however, it has been found that 81 per cent of the theoretical yield is the best obtainable, this being produced by using 90 per cent of the amount of H_2SO_4 (sp gr 1.824) specified and heating for 3 hr at 200°C. The reaction is carried out in horizontal cast-iron cylinders heated from the bottom. Careful fire control is important, inasmuch as the reaction itself develops a large amount of heat. Two leaden Wolf flasks connected in series are used to collect the HF. The product in the first one usually contains a small quantity of H_2SiF_6 which comes from the SiO_2 of the fluorspar. The second is water-cooled to condense the HF.

Hydrofluoric acid passes slowly through a lead tower filled with pure sand (99.5 per cent SiO_2), dissolving the SiO_2. The resultant H_2SiF_6 overflows into an oblong box containing granulated lead, where the reaction yields $PbSiF_6$. A copper centrifugal pump with a bronze shaft, submerged in the solution, provides the required circulation.

The electrolyte contains 5 to 10 per cent lead and 8 to 15 per cent total H_2SiF_6, the free H_2SiF_6 content being 3 to 5 per cent. Multiplying the lead value by 0.7 will give an approximate figure for the lead combined with H_2SiF_6. The electrical conductivities of $PbSiF_6$ and H_2SiF_6 are shown in Figs. 78 and 79. To ensure a solid cathode deposit, a hot strong solution of glue is added daily, to the amount of about 0.013 per cent of the weight of the electrolyte. This material is dissolved in hot water (10 per cent concentration) and added directly to each cell, so that all

cells receive due proportion once every 24 hr. The consumption of glue amounts to 1.5 lb (680 g) per ton of lead produced. By-product sulfonates are now replacing glue with success in some refineries.

The original electrolyte is colorless. It may appear slightly green from iron or nickel impurities or, on exposure to air, may take on a brownish color due to the presence of glue. The electrolyte demands frequent analytical control. Its acidity is reduced during operation and must be restored by adding fresh
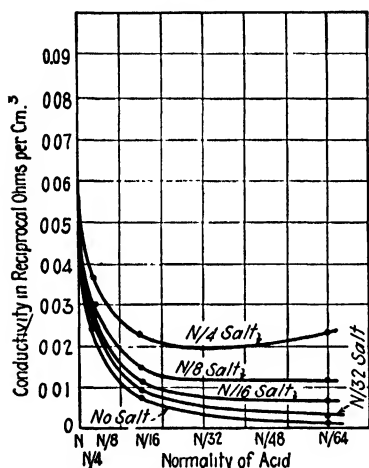
FIG. 78. Electric conductivity of H_2SiF_6 with different normalities of $PbSiF_6$ dissolved in the acid.
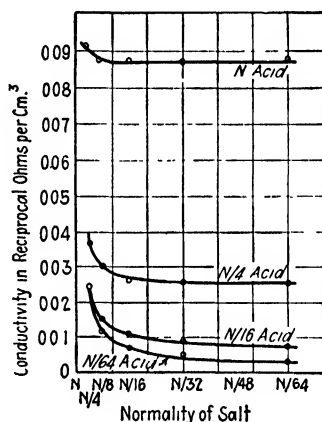
FIG. 79. Electric conductivity of $PbSiF_6$ when dissolved in different normalities of H_2SiF_6.

acid. The lead content normally increases; but should it become low, the electrolyte is passed over granulated lead. The refining process operates at a temperature of 35 to 46°C, although slight variations will not alter the type of deposit. They will, however, affect the conductivity of the solution as well as the condition of the asphalt lining of the tank. Too low a temperature will crack the coating, while one that is too high causes the lining to blister and soften. A copper coil in the head tank conducts steam in winter and cool water in summer for regulation of the temperature of the electrolyte.

Tanks. Tanks are arranged in double cascades. They are rectangular in shape with flat bottoms, being similar to those used in copper refining. In some refineries they are made of

wood, pitch coated, and in others of asphaltum-lined concrete. In the latter case the concrete is made of 1 part cement, 2 parts angular sand, and 3 parts of screened, well-washed, crushed, siliceous rock 1 to 2 in. in size. The tanks are lined with asphalt, usually of the petroleum-residue type having a melting point of 105°C, after the concrete has been given a priming coat with an asphaltum paint. The tank arrangement, busbar connections,

Fɪɢ. 80. Electrolytic lead tank room. (*Consolidated Mining and Smelting Company of Canada, Ltd.*)

inspection and control, and physical layout are somewhat similar to those of a copper refinery. A modern plant which is the result of the development of the original Betts installation is shown in Fig. 80.

If impure anodes be used, the rate of circulation of the electrolyte is 3 to 4 gal per min, while with pure anodes it becomes 7 gal per min. The solution is raised from the sump by means of copper centrifugal pumps equipped with monel metal wearing parts. An electrolyte loss of 5 to 10 lb H_2SiF_6 per ton of normal lead bullion is attributed in part to the dissociation of the acid. If the anodes contain appreciable quantities of impurities, the loss will approach the higher figure.

Anode Impurities and Current Density. Ordinarily, impurities in lead bullion do not total more than 2 per cent, 1 to 1.25 per

cent being antimony.   Anodes containing more than 2.25 per cent of foreign metals cause difficulties in electrolysis.   Silver in the cathodes must be kept as low as 2 to 7.5 ppm (2 to 7.5 mg per kg) of refined lead.   The usual impurities in the lead anodes are commonly present in such proportions that they will remain in the antimony slime sponge; copper is an exception.   Copper if present in excess of 0.04 per cent will form a hard skin on the surface of the anode insoluble in hydrofluosilicic acid.

At the Cerro de Pasco Copper Corporation at Oroya, Peru, the anodes run 90 to 95 per cent lead with a large amount of bismuth.   The refining method has been adapted to such an extent that highly impure anodes cause no difficulties.

The purity of the anode also controls the current density. With an anode analyzing Pb 66, Bi 7, Sb 19, As 5, Ag 2, Cu 1 per cent, Betts[20] used 4 amp per sq ft (0.4 amp per dm^2); whereas, in present-day refineries with anodes nearer 98 per cent lead, the current density is 16 to 18 amp per sq ft (1.7 to 1.9 amp per dm^2) of anode area.   With anode and cathode $1\frac{3}{4}$ in. apart, the tank voltage is 0.35 with new anodes; but owing largely to the accumulation of antimony sponge on the anode surface, this potential increases to as high as 0.7.   In ordinary operation tank voltages are between 0.35 and 0.6, varying with the current density and the age of the anodes.

Anodes and Cell Operation.   The anodes, cast in open molds, are made with shoulders which rest on the busbars of the tank when in position.   Data on refining, anode size, etc., are given in Table 43.   A thinner anode is used in lead refining as compared to the one found in copper refineries.   This is due to the fact that during electrolysis most of the impurities cling to the anode, increasing the resistance to the current.   An accumulation of such impurities may drop to the bottom of the tank, causing short circuits or, through solution or suspension, may be deposited at the cathode.

Cathodes are usually about $\frac{1}{2}$ to 1 in. larger than the anodes. Originally, sheet iron, plated with lead, was used as cathode. These were later replaced by sheets of electrodeposited lead.   In present practice cathodes are cast on sloping cast-iron tables fed by a trough at the upper end.

   [20] BETTS, A. G., "Lead Refining by Electrolysis," p. 56, John Wiley & Sons, Inc., New York, 1908.

The electrode spacing is $1\frac{3}{4}$ to $2\frac{1}{2}$ in., the usual range being $2\frac{1}{2}$ to $2\frac{1}{4}$ in. center to center and $1\frac{5}{8}$ in. face to face. The distance must be determined for the given conditions at the plant. Narrow spacings lessen the resistance and increase the kilowatt output but are conducive to short circuits and therefore to ampere-efficiency losses. Greater distances, on the other hand, although raising the ampere efficiency, tend to increase the resistance and increase the energy consumption per pound of lead deposited.

Anode corrosion is comparatively regular. Most of the impurities are insoluble, adhering to the anode. To ensure a full surface for these particles, about 25 to 35 per cent of the anode is left unattacked, returning to the anode kettles as scrap. The anode mud which may drop to the bottom of the tank is likely not only to cause short circuits, but also to set up a chemical reaction between its components and the free acid of the electrolyte. A 10-day cleanup and renewal of anodes is the practice at some plants, but with impure anodes 4-day replacement is common. The corroded anodes and their adhering slimes are taken from the tanks and deposited in a tank car about twice the size of the cell, filled with water. The mud is scraped away, the anodes being raised and lowered by means of an electric hoist. The anodes themselves are then brushed, either by hand or by rotary brushes, until clean, when they are raised, rinsed, and sent to the anode kettles. The slime is partly settled, then with the remaining electrolyte is passed through a filter press, washed with water, air-dried, and discharged for further treatment. A certain amount of lead will be held in the electrolyte in the pores of the anode mud even after washing. The first filtrate consists of electrolyte and goes to the head tank; the dilute and weaker portion is used for first water in the anode wash tanks. Filtration will remove most of the soluble lead, but the anode slimes will contain an appreciable percentage of insoluble lead. Anode mud analyses are given in the general table.

Anode Mud Treatment. The presence of bismuth, tellurium, and selenium is the determining factor in the treatment of the mud. If these metals be absent, the process is a simple one; but, with bismuth to be recovered, the treatment becomes complicated. The treatment of the anode residue slimes for the separation of the gold and silver content presents no unusual

TABLE 43. ELECTROLYTIC REFINING OF LEAD

	Cerro de Pasco Copper Corp., Oroya, Peru	Consolidated Mining and Smelting Company, Trail, B.C.	U.S.S. Lead Refinery, East Chicago, Ind.
Electrolyte:			
Sp gr	1 20–1 23	1 195–1 205	1 16
Pb, g/l	80–90	67–72	57 2
Total H_2SiF_6, g/l	120–140	140–150	110 1
Combined H_2SiF_6, g/l	55–63	46–50	40 3
Free H_2SiF_6, g/l	57	95–100	69 8
Temperature, °C	37	40–45	42–46
Circulation, gal/min	1–4	3–4	3–4
Circulation apparatus	Worthite pump	Monel rotary seal centrifugal pumps. Copper rotary immersion pumps	Copper centrifugal pumps
Current:			
Amp/sq ft cathode	16 5	24 anodes–22.3	14–16
Voltage per tank	0 46	0 35–0 5	0 35–0.44, last day 0.62
Current, kw per generator	6,000 amp, @ 125 volts	6,300 amp, @ 185 volts	4,700–5,100 amp, @ 105–120 volts
Current efficiency, %	90	93	93
Kwhr/lb	0.074 a.c.	0 09	0 0921
Anodes:			
Composition	93–96 % Pb, variable Ag, Au, Sb, As, Cu, Bi, Te	Pb 98.4%, Cu 0.05%, As 0.17%, Sn 0.004%, Bi 0.06%, Sb 1.2%	Sb 1.57%, Pb 98.00%
Length, width, thickness	36″ × 26″ × ¾″	30⅛″ × 26¼″ × 1¼″ submerged	3′0″ × 2′0″ × 1½″
Weight, lb	260, or 118 kg	430	470–475
Mode of suspension	Lugs	Cast lugs	Cast lugs
Life, days	4	6	10
Scrap, %	45	30	25–30
Cathodes:			
Starting sheet, length, width, thickness	36″ × 27″ × 1/32″	3′3″ × 2′2¾″ × 0.028″	3′1½″ × 2′4″ × 0.023″
Weight, lb	22	12	11
Mode of suspension	Cast integral to dovetailed cathode bar	Wrapped on Cu bars	3 strips folded over and spot-welded
Life, days	4	3	5
Weight, lb.	139, or 63 kg	150	173
Tanks:			
Length, width, depth	8′10″ × 2′7″ × 3′10″	8′9½″ × 2′6½″ × 3′8″	11′6″ × 2′6″ × 4′0″
Number of anodes, cathodes	24, 25	24, 25	28, 29
Electric connection	Walker	Great Falls (Anaconda) type	Walker
Materials of construction..	Reinforced concrete "Harvel" lining	Reinforced concrete, asphalt-lined	Concrete, asphalt, mastic-lined
Anode mud:			
Composition	Variable % of Ag, Au, Cu, Pb, As, Sb, Bi, Te	Au 0.004%, Ag 5.4%, Cu 2.3%, Sb 47.3%, As 6.4%, Sn 0.08%, Bi 3.0%, Pb 18.4%	Ag 15.35%, Au 0.32%, Pb 8–10%, Sb 45–55%, As 2–3%, Sn 0.058%, Cu 0.60%, Te 0.43%
Removed from anode after ? days	8	3 and 6	10
Removed from tank after ? days . . .	180	70	36

features. Variations in the method of treatment are based on the selective oxidation of the contained metals when heated in an oxidizing atmosphere. According to their ease of oxidation, the individual metallic constituents of the slimes follow the order As, Sb, Sn, Pb, Cu, Bi, Ag, and Au. The successful electrolytic work in the cell room demands that the cellular structure of the slime be not destroyed during its filtration and washing process.

At Trail, dewatered slimes contain 40 to 45 per cent moisture. These are fed directly to a melting furnace and heated in a reducing atmosphere so that oxidation may be prevented as far as possible. The maximum proportion of metal is produced together with the minimum amount of lead antimonite ($PbO \cdot Sb_2O_3$) slag. Arsenic is largely volatilized during this treatment and passes off with the furnace gases, to be c .ught in the collecting system. The slag is desilverized by the addition of coal and coke breeze, the resulting metal being added to the metal obtained from the slime treatment. The metals are then subjected to an oxidation heating whereby the antimony and arsenic are eliminated as oxide fumes which are collected. These form the initial product for the production of metallic antimony, the fumes running about 60 per cent Sb, 6 to 10 per cent As, 1 to 3 per cent Pb, and 2 to 20 oz Ag. All but about 7 per cent of the antimony in the metal can be removed by the oxidation treatment, and this remaining amount is eliminated by the formation of lead antimonite slags produced by the reaction of antimony oxide and lead oxide (litharge) with the resultant elimination of the greater part of the lead. At this point bismuth and copper are oxidized and form scoriae on top of the metal bath. These are constantly skimmed off so that about 80 per cent of the bismuth is removed from the metal, with the final production of doré or silver-gold alloy. The copper-bismuth scoriae or slags are the starting product for the recovery of bismuth. The doré metal is parted by the H_2SO_4 process. The gold sludge is remelted, cast into anodes, and refined electrolytically by the Wohlwill process. The small proportion of palladium contained in the lead ores may be recovered at periodic intervals from the gold-refining electrolyte.

Pure Lead. Electrolytic refining allows the production of unusually pure leads. In connection with his study of the effect

of impurities on the properties of metallic lead, Cowan[21] produced leads running purer than 99.999, of such high grade that 1,000-g analytical samples had to be taken for the determination of impurities.   Some of his results are given below.

ANALYSES OF LEAD BEFORE AND AFTER ELECTROLYTIC REFINING

Constituents	Original Southeast Missouri lead desilverized by Parkes process, %	Electrolytic refined second deposition, %
Silver..	0.0006	None (200 g)
Antimony	0.0020	0.00024 (1,000 g)
Copper	0.0003	0.000057 (1,000 g)
Iron..	0.0005	0.000193 (1,000 g)
Zinc....	0 0006	0.00008 (1,000 g)
Total impurities	0 0040	0 000570
Lead (by difference)	99 9960	99.999430

NOTE.—In the electrolytic refined lead, bismuth, tin, and arsenic are not present in amounts that could be called a trace, as determined on 100-g portion.

ANTIMONY

A number of different methods have been proposed and used at times for the electrolytic refining of antimony.   They included alkaline sulfantimonite solutions which gave pure antimony. The operations showed low current efficiency and difficulties with the formation of insoluble anode films.   Antimony chloride electrolytes were employed, but the cathode product always contained chlorine and chlorides which were explosive under certain conditions.   Fluoride solutions were used with better results.   The metal is refined in a combination sulfate-fluoride solution as given in Table 44 of operating data.   Antimony is less noble than arsenic, copper, and bismuth but more noble than tin and lead; hence, during refining, arsenic, copper, and bismuth go into the anode slimes, while tin and lead pass into solution.   In the presence of a large amount of H_2SO_4 in the electrolyte, lead is precipitated.

The raw materials for antimony are either anode muds from

[21] Private communication from William A. Cowan, National Lead Company.

lead refining, fumes from metallurgical operations, antimony slags from the treatment of copper anode muds, or antimony ores. The anode slimes produced during the refining are reworked by smelting with lead ores. Periodically part of the electrolyte is purified with insoluble anodes for the deposition of the antimony and by concentration and treatment with H_2SO_4 for the removal of the tin and iron. The antimony produced is 99.8 per cent pure.

TABLE 44. ELECTROLYTIC REFINING OF ANTIMONY

Electrolyte:	
Composition, g/l ..	Sb 25 to 30, Sn 100 to 110, Fe 11 to 12, H_2SO_4 200 to 300, HF 20
C.d... .	100 amp/m² (9.3 amp/sq ft)
Voltage	0 4
Anodes:	
Composition	Pb 2 to 6, Sn 3 to 6, Cu 0.5, Fe 0.5, As 0.05, . Sb 87 to 94%, Ag 7 oz/ton
Length, width, thickness	27 2″ × 19.7″ × 1.8″ (70 × 50 × 4.5 cm)
Weight	220 lb (100 kg)
Cathodes:	
Starting sheet	Copper
Composition. .	Pb 0.1, Sn 0.01, Cu 0.05, Fe 0.01, As 0.03, Sb 99.8%, Ag 0.4 oz/ton
Anode slime....	Pb 30 to 50, Sn 2 to 3, Cu 3 to 4, As 0.5, Sb 20 to 30%, Ag 70 to 85 oz/ton

BISMUTH

Bismuth-rich scoriae and slags are produced as a by-product of working up anode slimes from lead refining. These are treated by furnace methods. The residue is crude bismuth containing mainly silver and lead. This is refined electrolytically in an acid $BiCl_3$ solution containing somewhat more than 100 g HCl per liter and 3 to 4 g of bismuth in a Thum cell, the same type as used·for silver refining, at 50 to 60°C. The lead of the crude bismuth anode goes into solution as $PbCl_2$ but does not deposit with the bismuth. It concentrates in the electrolyte, portions of which are periodically removed and the $PbCl_2$ crystallized out.

Experimental refining of crude bismuth anodes containing 94 per cent Bi, 2.2 per cent Pb, 3.1 per cent Ag, 0.5 per cent Cu, 0.1 per cent Sb, 0.1 per cent Au, described by Mohn,[22] in an electrolyte containing 7 per cent bismuth as $BiCl_3$ and 9 to 10 per cent free HCl at anode current density of 18 to 19 amp per sq ft

[22] MOHN, A., *Electrochem. Ind.*, **5**, 314 (1907).

(2 amp per dm²) and cathode current density of 55 to 56 amp per sq ft (6 amp per dm²) at a bath voltage of 1.2, was not very satisfactory. Lead, antimony, copper, and, unless care were taken, some silver also dissolved. Silver enters the cathode deposit, while copper and antimony can be allowed to accumulate in the electrolyte only to a small extent.

Crude bismuth anodes containing silver and lead in bismuth fluosilicate electrolytes were found by Foerster and Schwabe[23] to give pure cathodic bismuth of a compact and dense nature. The silver remained undissolved in the slimes. The lead accumulated in the electrolyte. The single potentials of bismuth, silver, and lead against solutions of their fluosilicates are far apart.

IRON

Electrodeposition of iron dates back to 1846 when Bottger used a bath of $FeSO_4 \cdot 7H_2O$ and NH_4Cl. Bietz in 1869 produced electrolytic iron and employed it for making magnetic tests. Siemens[24] in 1889 proposed a general process in which sulfide-iron minerals were leached with ferric chloride or sulfate, the iron deposited from the leach liquors on a cathode in a diaphragm cell, and the leach regenerated. The first serious attempt to produce electrolytic iron in quantities was in 1904,[25] when the metal was deposited from a mixture of ferrous and ammonium sulfates at a current density of 6 to 10 amp per sq ft (0.65 to 1 amp per dm²) at 30°C and an average emf of 1 volt. In the plant of the Western Electric Company[26] the anodes were cast steel and the bath carried slightly on the alkaline side so that a considerable amount of oxides would be deposited in the cathode to make the latter brittle and easily ground up in connection with the manufacture of electrical "loading coils." It was not necessary to make a pure grade of iron. A further modification of the Burgess process was used by the Westinghouse Electric & Manufacturing Company[27] in which a pure grade of iron was produced for use in the manufacture of alloys for electromagnetic machinery and instruments. Commercially pure iron anodes

[23] FOERSTER, F., and SCHWABE, E., *Z. Elektrochem.*, **16**, 279 (1910).

[24] U.S. Patent 415,576.

[25] BURGESS, C. F., and HAMBUECHEN, C., *Trans. Am. Electrochem. Soc.*, **5**, 201 (1904).

[26] SPEED, B., and ELMAN, G. W., *J. Am. Inst. Elec. Eng.*, **40**, 596 (1921).

[27] BRACE, P. H., *J. Am. Inst. Elec. Eng.*, **44**, 922 (1925).

were used, but the refining range of the process was very small. Cathodic products would often be produced which were too high in either carbon or sulfur or both.

In 1914 an electrolytic iron plant was installed at Grenoble, France,[28] in which a hot neutral solution of ferrous chloride was employed as an electrolyte to which iron oxide was added as a depolarizer, with cast-iron anodes and rapidly rotating mandrels
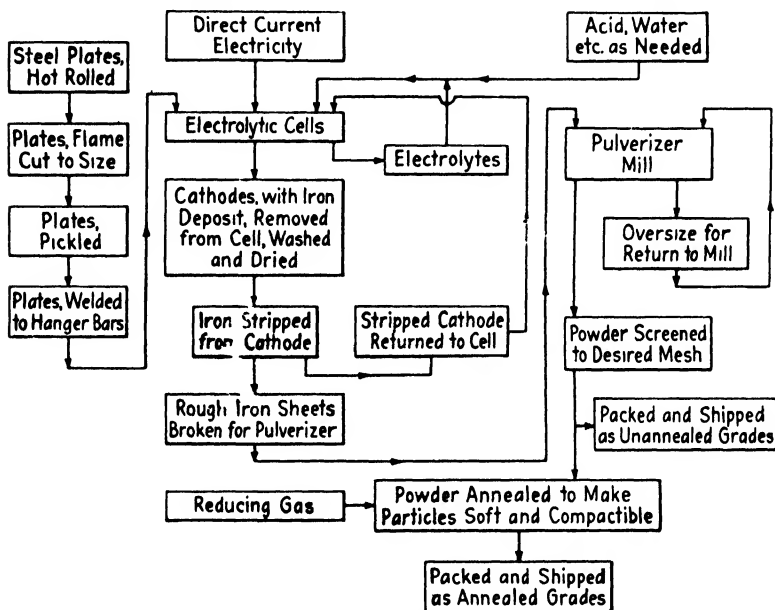
FIG. 81.   Electrolytic iron powder.

for cathodes.   Both tubing and plates were produced of electrolytic iron of good purity, showing Fe 99.967 per cent, C 0.008 per cent, Mn 0.009 per cent, P 0.002 per cent, Si 0.014 per cent, S trace.[29]   In commercial operation the electrolyte was circulated over iron turnings, and iron oxide was added; or else air was blown in to keep the H^+ ion concentration of the solution low. Current density was 93 to 105 amp per sq ft (10 to 11 amp per dm²) at a temperature of 80°C.   The small hydrogen content of

[28] GUILLET, L., *J. Iron Steel Inst.* (*London*) (1914); *Electrician*, **74,** 79 (1914); *Engineering*, **98,** 413 (1914).

[29] ESCARD, J., *Génie civil*, **75,** 165, 199, 225 (1919); *Elec. Rev.*, **76,** 610 (1920).

the metal was removed by annealing at 900°C.   Power requirements were of the order of 1.8 kwhr per lb.

A bath used in Germany, originated by Fischer,[30] contained 450 g $FeCl_2$, 500 g anhydrous $CaCl_2$, 750 g water, operated at 90 to 110°C at 93 to 185 amp per sq ft (10 to 20 amp per dm^2). Owing to the high working temperature, the iron deposited is relatively free from hydrogen and is therefore not brittle.   It

Fɪɢ. 82.   Cell room for production of electrolytic iron powder.   (*Plastic Metals.*)

has a purity of at least 99.95 per cent and can be deposited in thick, dense layers.

With the development of powder metallurgy, a demand for iron powder arose.   Part of this is met by electrolytic iron made by Plastic Metals at Johnstown, Pa., according to the flow sheet in Fig. 81, the operating conditions of which are tabulated in Table 45.[31]   The cell room is shown in Fig. 82, and the washing of the cathodes in Fig. 83 in which the structure of the deposit may be seen.

    [30] Fɪsᴄʜᴇʀ, F., *Z. Elektrochem.*, **15,** 595 (1909); Sᴛᴏʀᴇʏ, O. W., *Trans. Am. Electrochem. Soc.*, **29,** 357 (1916).
    [31] Private communication from B. T. du Pont, Plastic Metals, Johnstown, Pa.

TABLE 45. ELECTROLYTIC IRON POWDER

Electrolyte:
  Sp gr . . . .   1.1   .
  Percentage Fe. .   4.6 (50 g/l)
  pH... ....   4.5
  Temperature, °C   50
  Circulation, gal/min.   3.0
  Circulation apparatus   Centrifugal pumps
Current:
  Amp/sq ft..   25
  Voltage per tank......... . ... 2.5
  Current, voltage, and kw of generators   2,940 amp, 85 volts, 250 kw
  Current efficiency, %   .   .   90
  Kwhr/lb Fe.... . .   .   1.20
  Lb Fe per kw-day.   20.0
Anodes:
  Composition, % Fe.   . Steel plate, 99
  Length, width, thickness   . 24″ × 18′ × 1″
  Weight, lb. ...   120
  Mode of suspension   Welded to hanger bars
  Anode spacing, in   5
  Life, days......   12
  Scrap, %.... .   .   20
Cathodes:
  Length, width, thickness   18″ × 22½″ × 20 gage
  Weight, lb..   .   5½
  Mode of suspension..   Welded to hanger bars
  Replaced after ? days   .   2–3
  Weight, lb. ... .   15–22 lb, electrolytic Fe
Manipulation of electrodes   By overhead crane
Deposition tanks:
  Materials of construction.   Haveg
  Length, width, depth .. .   10′ × 30″ × 30″
  Number of anodes, cathodes   .   21, 20
  Electric connection.... . .   .   Series
  Amp/sq in. cross section of busbar..   1,000
Anode mud:
  Percentage of anode ..   17
  Composition........   . .   Metallic iron and other metal
                                     oxides and sulfates
  Removed after ? days..   . .   . 8

MERCURY

Newbery and Naude[32] refined mercury in a $HgClO_4$ electrolyte with a mercury cathode at a current density of 9.2 amp per sq ft with a cell voltage of 0.5 volt.

[32] NEWBERY, E., and NAUDE, S. M., *Trans. Electrochem. Soc.*, **64**, 189 (1933)
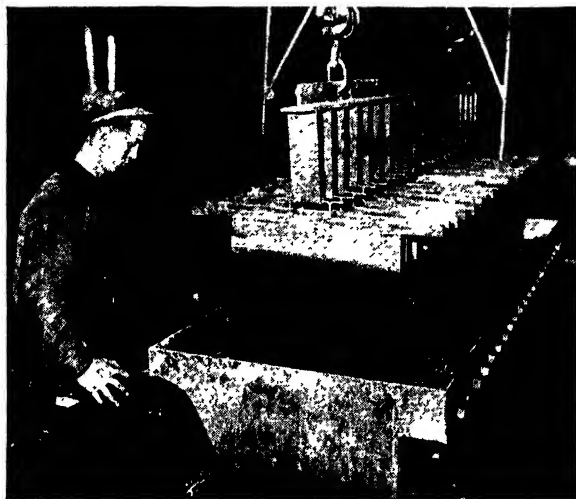
Fig. 83. Washing of cathodes in the production of electrolytic iron powder. (*Plastic Metals.*)

SOLDER

Hermsdorf and Heberlein[33] described the electrolytic refining of lead-tin alloys using a lead-tin fluosilicate electrolyte. The electrolytic process has the advantage of removing in one operation both the base impurities and the precious metals to a greater extent than is possible by ordinary methods.[34] The operating data of the plant are tabulated in Table 46.

TIN

During the First World War the electrolytic refining of tin was developed in the United States as a means of dealing with the metal obtained from the smelting of complex or impure Bolivian ores from which straight dry thermal methods of refining produced a poor grade of metal.

Electrolytes. Many electrolytes for tin refining have been proposed. Some of them have been used on a commercial scale, others have found application only for plating, and a multitude of others so violated commercial considerations that they

[33] HERMSDORF, R. P. E., and HEBERLEIN, M., *Trans. Am. Inst. Mining Met. Engrs.*, **121**, 289 (1936).

[34] U.S. Patent 1,842,028 (1932).

TABLE 46. ELECTROLYTIC SOLDER

Electrolyte:
Pb, g/l	25–35
Sn, g/l	30–45
Free H_2SiF_6, g/l	60–70
Total acid, g/l	130–150
Sp gr	1 18–1.20
Temperature, °F	105
Addition agents	Glue
C.d., amp/sq ft cathode area	15
Voltage drop between electrodes	0.34
Current efficiency, %	90–96

Anodes:
Material	Impure solder, average analysis 62 Pb, 35 Sn, 2 Sb, 0.25 As, 0.25% Cu; 0.05 oz Au per ton, 30 oz Ag per ton
Size	$36'' \times 24'' \times 1\frac{1}{4}''$
Weight, lb	350–400
Replaced after ? days	10

Cathodes:
Material	Electrolytically refined solder
Size	$38'' \times 26''$
Removed after ? days	5
Number anodes, cathodes	31, 32
Anode spacing, in	$4\frac{1}{2}$
Anode scrap, %	25

Deposition tanks:
Material of construction	Concrete, lined with pitch and mastic mixture
Length × width × depth	$11' 6'' \times 2' 6'' \times 3' 9''$

have never been used. Mantell[35] has summed up the various baths proposed.

The bath employed commercially at the plant of the American Smelting and Refining Company at Perth Amboy from 1917 to 1923 was considerably changed as its development proceeded. It originally contained 15 per cent of H_2SiF_6, 4 per cent Sn, with H_2SO_4 added as a lead precipitant. It was later changed to a H_2SO_4 base electrolyte containing 8 per cent H_2SO_4, 4 per cent cresol-phenol sulfonic acid, and 3 per cent Sn.

Anode Impurities. Tin is in a desirable position in the electromotive series of the metals for electrolytic refining. The only impurity of frequent occurrence that stands equal or close to tin and would dissolve is lead, all the others being below tin.

[35] MANTELL, C. L., "Tin," Chemical Catalog Company, Inc., New York, 1929; 2d ed., Reinhold Publishing Corporation, New York, 1949.

Practically, lead is the only impurity that dissolves; consequently the electrolyte must contain a radical that will form an insoluble compound with lead, such as a sulfate, chromate, fluoride, etc. The other metals occurring as impurities in tin (arsenic, antimony, bismuth, copper, etc.) are not dissolved and remain in the anode slimes.

Cell Operation. The requirements that a tin electrolyte should meet are: (1) It must readily dissolve tin from the anode and thus prevent the anode from becoming passive or insoluble, with consequent high voltage and polarization; (2) it must be a good conductor of electricity; (3) the cathode deposit must be adherent.

Tin is a very crystalline metal, and the cathode deposit from most electrolytes consists of long dendritic or needlelike crystals. These crystals are loosely attached and grow rapidly, touching the anode and causing short circuits. The tin deposits for satisfactory work should be smooth, dense, and adherent. To obtain such a deposit from most tin electrolytes, an addition agent is necessary.

The operating data of the Perth Amboy plant are given in Table 47. The total acid in the electrolyte is calculated as H_2SO_4, although it was partly H_2SO_4 and partly cresol sulfonic acid. Glue-cresylic acid emulsions were used as addition agents. The addition agent consumed was of the order of $\frac{1}{3}$ to 3 lb of glue and 8 to 16 lb of cresylic acid per ton of refined tin. Refinery starting sheets were made by pouring molten electrolytic tin over an inclined steel table of the size and shape of sheet desired, a method similar to that used for making starting sheets for the electrolytic refining of lead. The electrolytic tin produced analyzed better than 99.98 per cent Sn.

Recovery of Tin from Tin-plate Scrap. As the tin-plate industry grew to large proportions, the problem arose as to the disposal of clippings and other scrap which accumulate in large quantities. Tin-plate scrap is a result of the working up of tin plate into cans, boxes, containers, etc. In its plated state, the scrap cannot be puddled or charged into the open-hearth furnace. The tin coating prevents the making of a satisfactory iron or steel product.

As far back as 1876 Keith[36] recommended the electrolysis of

---

[36] KEITH, N. S., U.S. Patent 179,658.

TABLE 47. ELECTROLYTIC REFINING OF TIN

Electrolyte:
- Percentage Sn . .   . 3·
- Percentage total acid (as H_2SO_4) .   . 10.2
- Temperature, °C   .   35
- Circulation, gal/min   . .   5
- Circulation apparatus.   . . . . Vertical centrifugal pumps

Current:
- Amp/sq ft cathode   8–10
- Voltage per tank   .   . . 0 3–0 35
- Current, kw per generator 4,500
- Current efficiency 85%
- Kwhr/lb Sn .   . . 0 085

Anodes:
- Composition.   Sn 96.0, Bi 1.0, Sb 0.25, As 0.15, Cu 0.25, Pb 1.0%
- Length, width, thickness   . $33'' \times 36'' \times 1\frac{1}{4}''$
- Weight, lb   350
- Mode of suspension   Cast lugs
- Life, days .   21
- Scrap, % .   25

Cathode:
- Starting sheet, length $\times$ width $\times$ thickness $34'' \times 37'' \times \frac{5}{16}''$
- Weight, lb   . 8–10
- Mode of suspension   . Wrapped
- Replaced after ? days   7
- Weight, lb   100

Deposition tanks:
- Length $\times$ width $\times$ depth $12'11'' \times 3'5'' \times 3'6''$
- Number anodes, cathodes   26, 27
- Electric connection   Walker
- Material of construction   Wood, lead-lined

Anode mud:
- Percentage of anode   5
- Composition . . .   Pb 20, Cu 5, As 3, Sb 5, Sn 30, Bi 20%

tin scrap in an alkali solution, while in 1882 Theodor Gold-schmidt, in Germany, conducted experiments with a warm solution of caustic soda, using the tin-plate scrap as the anode and an iron plate as cathode. The operation on a plant scale offers difficulties, both electrochemical and mechanical, which have been solved in commercial operation.

The tin is recovered at the cathode in the form of a spongy or finely granulated precipitate, which can be removed and melted. The process yields a serviceable iron which may be compressed into solid billets and for which a market can be readily found.

The tin-plate scrap serves as the anode of the cell; the cathodes are either steel plates or the sides of the steel tanks. Iron is the cheapest and the most generally used electrode material. The tanks are connected up to the negative conductor, while the positive part of the cell is connected to bars or tubes which are placed in insulated supports lying along the edges of the tanks. The baskets are charged with tin-plate scrap and are of suitable size and dimensions so that they may be handled with ease. The baskets are made of heavy, iron-wire gauze of wide mesh, bound with strong heavy angle-iron bands. The bands extend up from the basket and are bent into hooks above, which rest on and make contact with the positive busbars. The basket design is usually on the basis of about 3 to $3\frac{1}{2}$ lb of scrap per cubic foot of basket volume. Baskets fit the tanks rather closely, with enough clearance between the sides of the baskets and the inner walls of the tanks or the cathodes to prevent electrical short circuits. The capacity of baskets bear about a 3:5 relation to the volume of the bath. The electrical resistance of the electrolyte is thus kept as low as possible. The baskets are suspended side by side.

The insertion and removal of the scrap baskets in the electrolyte take place in a regular and systematic manner. The completion of the detinning can be checked by the change in color of the scrap from its original appearance to colors varying from blue black to red brown.

The detinned scrap is allowed to drain from the electrolyte and is washed with water. The material is then dumped out of the baskets, dried, and compressed for shipment.

At intervals the tin sponge is removed from the cathode plates by iron scrapers, the cathodes being lifted out of the cells at the time. The sponge tin is washed free from alkali with water. It is dried by centrifuging and melted to massive tin.

Tin-bearing slimes at the bottom of the electrolytic baths, and material dropping into the bath when the cathodes are scraped, are produced. This material contains tin, sand, iron, alkali, and various organic substances introduced into the bath through dirt on the scrap. The slimes are recovered by draining them off at intervals, adding them to slimes resulting from the detinned scrap washing tanks and the tin oxide produced by regenerating the electrolyte. The whole mass is smelted for tin.

CHAPTER 16

ELECTROWINNING

COPPER

In several places in the world, copper-containing minerals are treated for the recovery of the copper by electrowinning methods in which the mineral is leached or dissolved by a solution which, in turn, becomes an electrolyte and is stripped of a portion of its metal values by electrolytic precipitation, the stripped or spent electrolyte being returned for leaching fresh ore in a cyclic process. The metallic values of ores treated by electrowinning methods are usually very low, being of the order of 1.5 to 1.75 per cent copper or less. At the plant of the Chile Copper Company at Chuquicamata, Chile, the principal copper minerals are chalcanthite ($CuSO_4 \cdot 5H_2O$), brochantite ($CuSO_4 \cdot 3Cu(OH)_2$), and atacamite ($CuCl_2 \cdot 3Cu(OH)_2$), and the leach contains H_2SO_4.

In the plant of the Inspiration Consolidated Copper Company at Inspiration, Ariz., the ore consists of mixed oxides and sulfides in which the total copper of the ore is of the order of 1.1 to 1.2 per cent. The leach is a H_2SO_4-$Fe_2(SO_4)_3$ solution and the insoluble anodes are 8 per cent antimonial lead. Modified leaching methods are employed in which the oxide is removed from the ore by H_2SO_4 solutions and the sulfide recovered by flotation from the leached ore.

In general the ores are leached in large concrete tanks. At Chile the tanks are of reinforced concrete lined with mastic, while at Inspiration they are reinforced concrete lined with lead. Despite the fact that hydrometallurgical plants are working on extremely low-grade ores, the copper recovery is of the order of 80 to 90 per cent, and the production costs are considerably lower than in pyrometallurgical plants operating smelters. These smelters in addition have the advantage of high copper content ores to be worked. The commercial plants in operation were preceded by a large amount of pilot-plant work.[1]

[1] Morse, H. W., and Tobelmann, H. A., *Trans. Am. Inst. Mining Met. Engrs.*, **55**, 830 (1916); Tobelmann, H. A., and Potter, J. A., *ibid.*, **60**, 22 (1919); Sullivan, J. D., *ibid.*, **106**, 515 (1933).

Ore Leaching. Chile Copper Company. The methods employed at the plant of the Chile Copper Company and at the New Cornelia Mines of the Calumet and Arizona Mining Company at Ajo will be discussed. A typical composite analysis of the ore treated at Chuquicamata shows Cu 1.58 per cent, SiO_2 66.10 per cent, Fe 1.41 per cent, CaO 0.20 per cent, Al_2O_3 17.70 per cent, MgO 0.68 per cent, S 2.10 per cent, HNO_3 0.03 per cent, Cl 0.05 per cent, Na 0.80 per cent, K 4.80 per cent, Mn 0.07 per cent, Mo 0.01 per cent, As 0.005 per cent, Sb 0.005 per cent, Ba 0.01 per cent, H_2O 0.70 per cent, O in sulfates 3.94 per cent. Eichrodt[2] says that the most important constituents of the ore are (1) the total copper content; (2) the acid-insoluble copper which directly affects the extraction, as the leach used recovers practically no acid-insoluble copper; (3) the copper in the form of acid-making copper mineral such as chalcanthite ($CuSO_4 \cdot 5H_2O$); (4) the chlorine content which must be removed from the leaching solutions before they enter the electrolytic tank house; (5) the nitrates, in that HNO_3 in leach liquors determines the materials of construction necessary, affects the insoluble anodes used in electrolytic precipitation, oxidizes the iron in the solution to the ferric state, and itself will dissolve cathode copper; (6) the soluble iron which in the leaching solution will have a tendency to oxidize to the ferric state and, as such, attacks the cathode copper, or as the result of the alternate oxidation at the anode and reduction at the cathode, affects current efficiency; (7) the soluble molybdenum which appears to aggravate the oxidizing effect of the HNO_3 on the iron, as well as increase the effect of the HNO_3.

In general the ore is mined by surface workings employing blasting and steam-shovel methods. It is delivered to the plant and crushed in such a manner that most effective leaching of its metallic constituents may be done.[3] The crushed ore is charged into large concrete leaching vats or tanks. Sometimes the ore is charged into leaching solution already in the tank, and sometimes the solution is introduced into the vat after part or all of the ore has been charged. An attempt is made to have the operation of ore charging and filling of the tank with solution finish at the

[2] EICHRODT, W., The Leaching Process at Chuquicamata, Chile, *Trans. Am. Inst. Mining Met. Engrs.*, 186, (1930).

[3] CAMPBELL, T. C., Chile Exploration Co., Chuquicamata Reduction Plant, *Trans. Am. Inst. Mining Met. Engrs.*, 106, 559 (1933).

same time, so that a maximum soaking period of the ore in the leaching solution may be obtained. At the Chile plant the smaller tanks have an average charge of about 10,600 short tons of ore and the larger ones about 11,950.

The leaching operation takes place in two stages. In the first the copper is dissolved from the ore. The second stage consists of washing or displacing from the leached ore the dissolved values or water-soluble copper that remain. The first stage consists of a countercurrent treatment by two solutions. The first solution on the ore is introduced from the bottom of the vat and percolates upward until the ore is saturated and covered with liquor. This so-called treatment solution is normally relatively low in copper and high in free acid. After a soaking period, this solution or a portion of the amount originally used in covering the ore is drawn off at the bottom of the tank. It has been enriched in copper and its acidity reduced due to the formation of $CuSO_4$. It is now termed "strong solution." As it is withdrawn from the leaching tank, it is displaced by spent electrolyte from the tank house at a rae sufficient to keep the ore in the leaching vat covered. The spent electrolyte is low in copper and high in free acid. It may be defined as strong solution which, after partial electrodeposition of its copper content, is returned to the leaching plant for reenrichment. Its copper content is normally about 5 g per liter. The process of withdrawal of strong solution is interrupted after a time and the ore allowed to soak, after which period more strong or enriched solution is produced, being displaced as before by spent electrolyte. A number of such soaking periods may occur in the leaching treatment. Finally the ore is allowed to soak in the displacing solutions until it is necessary to wash, the solutions produced during the first part of washing being used in the treatment of another charge of ore. All solutions except those used in first covering the ore are put on top of the vat, and the solutions they displace are withdrawn at the bottom. The solutions produced at the start of the process of washing the ore are termed "treatment solutions" and are used for the treatment of unleached or partially leached ore.

Strong solution, resulting from the leaching of the ore, is high in copper, low in acid, and is sent to the tank house for electrodeposition of part of the copper content. Its metal and acid content depend upon the constituents of the ore treated, the

soaking periods, the content of the solutions from which the strong solution was produced, and the order of the batch in production. Batches of strong solution from one charge are mixed with those from other charges before they are sent to the tank house via the dechloridizing plant. In this manner an even grade of solution results, averaging about 35 g per liter of copper.
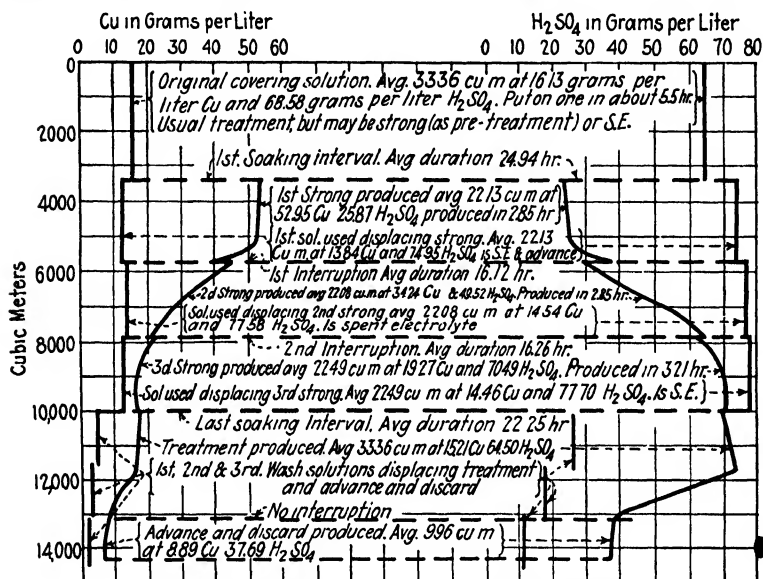
Fig. 84. Behavior of strong solution during production.

Eichrodt[4] has summed up the behavior of strong solutions during production in Fig. 84, describing the results shown in the curves as follows:

The contents of the first strong is practically constant until 53 per cent of the volume covering and saturating the ore has been produced. At this point the copper content of the solution commences to drop, because the displacing solution is coming through the charge mixed with the enriched solution faster than it is dissolving copper from the ore. After the interruption, the second strong starts off with a copper content a little higher than the finish of the first strong, but this content drops off rapidly, since the values in the solution on the charge appear to remain dispersed after the production of the first strong. There is also a slight pick-up at the start of producing third strong and at the start of

[4] EICHRODT, *loc. cit.*

the treatment, and both of these solutions appear to have been on the charge in layers with the strongest solution at the bottom of the vat. The drop in the value of the copper in the third strong becomes more gradual as this value approaches that in the spent electrolyte. This strong is interrupted when the copper content reaches 18 g per liter, which results in the subsequent production of a treatment solution of about the same copper content as spent electrolyte. It can be seen that after the production of second strong, the process is practically a displacing or diluting of the enriched solutions, or a washing process.

Electrolyte and Leach Liquors. Before electrolysis the leaching liquors are dechloridized by agitation with cement copper for the production of insoluble CuCl. At the same time the ferric salts are reduced by the copper. Table 48 gives the analysis of strong solution from the leach plant when sent to the dechloridizing plant, after dechloridizing when it is sent to the tank house,

TABLE 48

	Cu, g/l	H_2SO_4, g/l	Cl, g/l	Total Fe, g/l	Ferric Fe, g/l
Strong solution from leach plant to dechloridizing plant	35 39	47 85	0 59	4 60	1 37
Strong solution from dechloridizing plant to tank house	36 19	46 09	0 13	4 62	0.01
Spent electrolyte returned from tank house to leaching plant	14 44	78 54	0.21	4 60	1 13

and the spent electrolyte returned to the leaching plant. Spent electrolyte is a very complex solution, as shown by the typical composite analysis:

	g/l		g/l		g/l
Cu	14 44	Al.	1.75	K	2 30
Acid	78.54	As	0 242	Pb.	0 011
Cl	0 21	Sb	0 009	Sn	0.004
Fe	4 60	Ca	0 475	Mn	0 135
SO_4	144 83	Mg	0 147	Mo	0 248
HNO_3	3.12	Na	6 74	Total solids	197.78

With the continued leaching, the concentration of iron, HNO_3, and molybdenum in the leaching liquors will build up. To diminish this and control it, portions of the electrolyte are discarded either continuously in small amounts or at regular inter-

vals. As a result, a certain amount of total available acid concentration is sacrificed. At the Chile plant it has been practicable to control the constituents of the primary solution system by solution discard alone and without the addition of H_2SO_4, in that the ore furnishes acid-forming constituents. Operating data for the leaching and electrolytic deposition of copper are given in Table 49.

Metal Precipitation. The electrolytic precipitation of the copper is done in a plant which is quite similar to a copper refinery, save that insoluble anodes are used. The insoluble Chilex anode consists essentially of an alloy of copper, silicon, iron, and lead with small amounts of tin and other metals. The anodes are cast in a five-bar grid form. Another portion of the plant uses antimony-lead anodes. The flow sheet of the electrolytic tank house shown in Fig. 85 is much more complex than that of a copper refinery.[5] The starting sheets may be made either from strong electrolyte with insoluble anodes or from soluble copper anodes in the same manner as in the copper refinery. Cathodes are produced from the electrolytes that are reduced in copper content and increased in acidity during the operation for return to the leaching plant, as well as from spent or discarded solutions where the cathodes are produced as the result of plating down. Cement copper is produced in the final metal recovery from waste electrolyte. The marketable copper produced from the deposition tanks runs 99.96 per cent Cu and shows a conductivity on the International standard of 98.7 for the hard copper and 100.9 for the annealed.

Ore Leaching at Inspiration. At the Chile Copper Company plant, the leaching solution is practically one of H_2SO_4 which is without effect on the sulfide content of the ore. At the plant of the Inspiration Consolidated Copper Company at Inspiration, Ariz.,[6] mixed oxide and sulfide copper ores were leached by ferric sulfate solutions. A deliberate effort was made to maintain the ferric-sulfate concentration in the leaching solution at a point high enough to dissolve the large amount of copper contained in the ore as chalcocite (Cu_2S). This necessitated carrying a high percentage of total iron in solution, even though a high

   [5] CAMPBELL, *loc. cit.*
   [6] *Eng. Mining J.*, **128**, 612 (1929); ALDRICH, H. W., and SCOTT, W. G., *Trans. Am. Inst. Mining Met. Engrs.*, **106**, 650 (1933).

concentration of ferric sulfate is disadvantageous to high current efficiencies in the tank house. A balance was maintained between the necessary strength of ferric sulfate for copper sulfide extraction and the loss of current efficiency in the tank house by manipulation of solutions and their concentration. General practice has been to hold the average concentration of
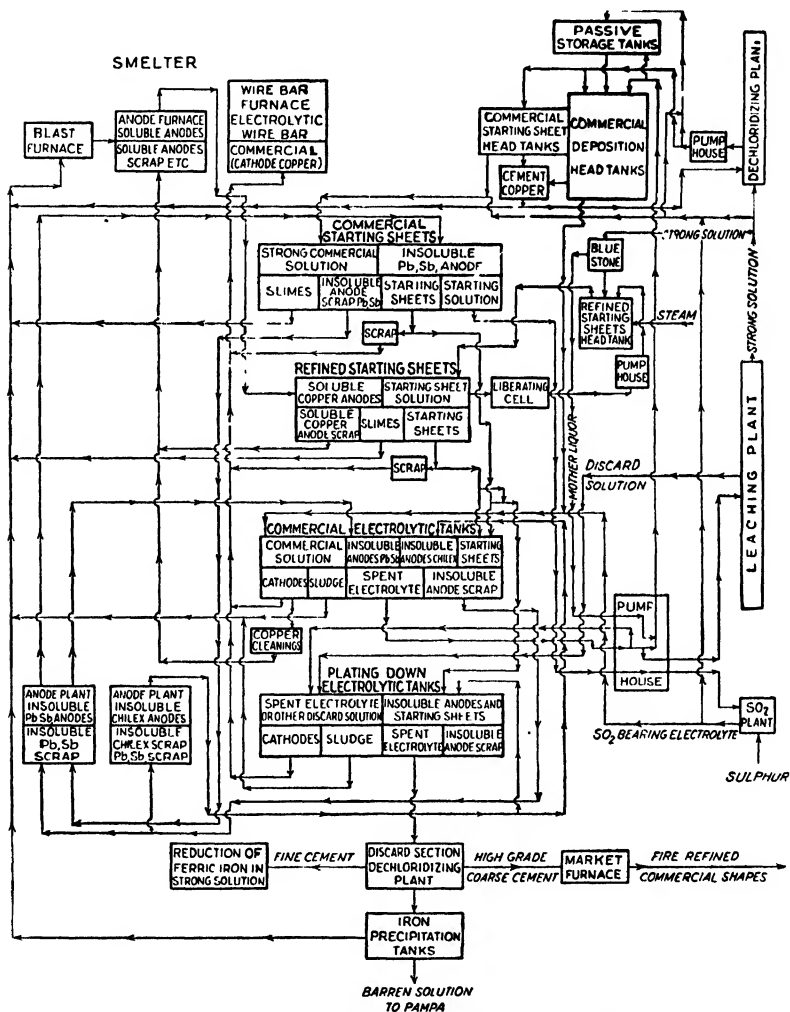
Fɪɢ. 85. Flow sheet of electrolytic tank house.

TABLE 49. ELECTROWINNING OF COPPER

Chile Exploration Company, Chuquicamata, Chile

	Starting sheets		Deposition tanks			
	Commercial	Refined	1st stage, 70,093	2d stage, 19,491	Plating down, 3,638	Whole house, 93,222
Electrolyte to cells:						
Sp gr	1 130	1 225	1 115	1 110	1 110	1 114
Cu, g/l	38 921	52 10	24 96	20 28	17 36	23 69
Total H₂SO₄, g/l	93 76	201 54	94 74	96 19	85 22	94 67
Free H₂SO₄, g/l	35 38	123 39	57 30	65 77	59 18	59 14
Cl, g/l.	0 049	0 04	0 09	0 09	0 12	0 09
Total Fe, g/l	2 81	3 44	2 87	2 82	2 69	2 85
Ferric Fe, g/l			1 16	1 69	1 05	1 26
Ferrous Fe, g/l			1 71	1 13	1 64	1 59
Temperature, °C	28 3	47 6	32 6	34 2	33 4	33 4
Electrolyte from cells:						
Sp gr	1 127	1 225	1 110	1 105	1 095	1 108
Cu, g/l	35 766	52 10	19 71	15 96	5 78	18 38
Total H₂SO₄, g/l	93 75	201 54	95 51	94 98	85 22	95 07
Free H₂SO₄, g/l	40 10	123 39	65 95	71 04	76 55	67 50
Cl, g/l	0 049	0 04	0 09	0 10	0 12	0 09
Total Fe, g/l	2 88	3 44	2 83	2 83	2 69	2 82
Ferric Fe, g/l	0 73		1 88	1 95	1 70	1 88
Ferrous Fe, g/l	2 15		0 95	0 88	0 99	0 94
Temperature, °C	29 5	47 6	36 0	36 4	39 3	36 2
Current:						
Total	25,319	25,080	24,538	23,155	26,957	24,538
C.d., amp/sq ft	16	21 2	14 20	13 40	15 60	14 87
Current efficiency, %	86 89	84 79	85 53	84 05	81 13	84 00
Voltage per tank	2 12	0 46	2 00	1 96	2 02	2 00
Kwhr/lb Cu	0 932	0 208	0 891	0 892	0 951	0 900
Lb Cu per kw-day	25 76	115 42	26 80	26 91	25 24	26 67
Anodes:						
Material	Pb-Sb-Ag	Soluble anode	Pb-Sb-Ag	Pb-Sb-Ag	Pb-Sb-Ag	Pb-Sb-Ag
Length, width, thickness	4'2¼" × 3'1¼" × 0.35"	4'3¾" × 3'13,"	4'1" × 2'9" × 0.35"	4'1" × 2'9" × 0.35"	4'1" × 2'9" × 0.35"	4'1" × 2'9" × 0.35"
Spacing	3	4½	3	3	3	3
Weight, lb	310	789	210	210	210	210
Mode of suspension	Cu insert	Cast Cu lugs	Cu insert	Cu insert	Cu insert	Cu insert
Life in days		19				
Scrap, %		20				

TABLE 49. ELECTROWINNING OF COPPER.—(Continued)

Chile Exploration Company, Chuquicamata, Chile

	Starting sheets		Deposition tanks			
	Commercial	Refined	1st stage, 70,093	2d stage, 19,491	Plating down, 3,638	Whole house, 93,222
Cathodes:						
Material	Cu blank	Cu blank	Cu sheet	Cu sheet	Cu sheet	Cu sheet
Length × width × thickness	4'1" × 3'1" × ¼"	4'1" × 3'1" × ¼"	3'0" × 4'0"	3'0" × 4'0"	3'0" × 4'0"	3'0" × 4'0"
Weight, lb	150	150	150	150	150	150
Mode of suspension	Riveted to bar	Riveted to bar	2 loops punched	2 loops punched	2 loops punched	2 loops punched
Replaced after ? days	Stripped daily	Stripped daily	5–8	5–8	5–8	5–8
Weight starting sheet, lb	11	16	11	11	11	11
Per cent starting sheets used for loops, scrap, etc	19	19	19	19	19	19
Deposition tanks:						
Number, average	72 48	30 73	616	152	67 67	835 67
Length × width × depth	19'2" × 3'11" × 4'10"	19'2" × 3'11" × 4'10"	19'2" × 3'11" × 4'10"	19'2" × 3'11" × 4'10"	19'2" × 3'11" × 4'10"	19'2" × 3'11" × 4'10"
Number of anodes, cathodes	63, 62	48, 47			73, 72	73, 72
Electric connection	Whitehead	Walker	Whitehead	Whitehead	Whitehead	Whitehead
Material of construction	Mastic-lined concrete	Mastic-lined concrete	Mastic-lined concrete	Mastic-lined concrete	Mastic-lined concrete	Mastic-lined concrete
Circulation, gal/min	36 41	3–5	334	376	333 7	342
Method of leaching			Batch percolation			
Leaching vats:						
Material of construction			Reinforced concrete lined with 4" of 27%, asphalt sand mixture			
Length × width × depth			150' × 110' × (14' and 19.5')			
Average charge per tank, tons			13, 13'			
Circulation, gal/min			3,000			
Ore:						
Per cent Cu				1.809		
Per cent Cu, acid soluble				1.477		
Per cent oxide Cu				1.477		
Per cent sulfide Cu				0.332		
Tailings:						
Total per cent Cu				0.343		
Per cent water-soluble Cu				0.030		
Per cent oxide Cu, acid-soluble				0.056		
Per cent sulfide Cu				0.287		
Extraction:						
Per cent total Cu				81.963		
Per cent oxide Cu				96.357		
Per cent sulfide Cu				17.880		

TABLE 49. ELECTROWINNING OF COPPER.—(Continued)

	Inspiration Consolidated Copper Co., Inspiration, Ariz.		Andes Copper Mining Co., Potrerillos, Chile		Union Minière du Haut Katanga, Katanga, Belgian Congo	
	Starting sheets	Deposition tanks	Starting sheets	Deposition tanks	Starting sheets	Deposition tanks
Electrolyte to cells:						
Sp gr		1 209	1 238	1 133		1.270
Cu, g/l	30-40	31 1	46 8	29 3	35-40	66
Total H_2SO_4, g/l	120-150	20 1	166 6	30 0	105	6.7
Free H_2SO_4, g/l						
Cl_2, g/l			0 003	0 07		2.5
Total Fe, g/l		20 5	3 18	2 24		1.5
Ferric Fe, g/l		5 7	0 10	0 22		1.0
Ferrous Fe, g/l			3 08	2 02		
Temperature, °C	55	35.8	56 2	29 5		30
Electrolyte from cells:						
Sp gr			1 248	1 106		
Cu, g/l		26 4	46 6	10 65		62.1
Total H_2SO_4, g/l		28 9	167 6	60 4		
Free H_2SO_4, g/l						
Cl_2, g/l			0 006	0 08		2.5
Total Fe, g/l		12 0	3.30	2 10		1.3
Ferric Fe, g/l			0 05	1 16		1.2
Ferrous Fe, g/l			3 25	0 94		
Temperature, °C		41 8	48.7	38 5		55
Current:						
Total					20,000 amp (See note 1)	20,000 amp (See note 1)
C.d., amp/sq ft	14-16	11 4	15 93	9 78	16	16
Current efficiency, %		71 65	92 69	83 95	90-92	90-92
Voltage per tank		2 16	0 359	2 066	0.6 × 3 = 1.8	2.05 − 2.2 × 3 = 6.1 − 6.6
Kwhr/lb Cu		1 347	0.168	1 082	0 275	0 93
Lb Cu per kw-day			161 92	25 229		25 8
Anodes:						
Material	Blister Cu	8% Sb lead	Blister Cu	83.5 Pb, 15.0 Sb, 1.3 As, 0.15 Cu	Cast copper	6% Sb hard lead
Length, width, thickness		3'2" × 3'4" × ½"	3'3¼" × 2'2½"	3'3¼" × 2'2½"	3'9⅜" × 2'9¼" × 1⅜"	3'9 15/16" × 2'5 7/8" × 7/16"
Spacing		4 0	4½"	3½"	4¾" = 120 mm	3½" = 90 mm
Weight, lb	1,100	340	550-600	200	78½	250
Mode of suspension			Cast lugs	Cast lugs Corrosion equals 2 lb of anode/ton of Cu deposited	Cast lugs	Copper bar, cast in
Life in days			35		15-20	
Scrap, %	22 0		18		20-25	

TABLE 49. ELECTROWINNING OF COPPER.—(*Continued*)

	Inspiration Consolidated Copper Co., Inspiration, Ariz.		Andes Copper Mining Co., Potrerillos, Chile		Union Minière du Haut Katanga, Katanga, Belgian Congo	
	Starting sheets	Deposition tanks	Starting sheets	Deposition tanks	Starting sheets	Deposition tanks
Cathodes:						
Material	Rolled Cu		Rolled Cu sheet	Start. sheets	Cu blanks	Cu starting sheets
Length × width × thickness	3'9" × 3'6"	3'8" × 3'6"	2'4¾" × 3'7⅜"	2'4" × 3'1½"	3'11½" × 2'10¼" × 3/16"	3'5¼" × 2'9¼"
Weight, lb		100	80	68 48		110-120
Mode of suspension	....	Punched loops	Riveted bars	2 loops	Riveted copper bars	Punched loops
Replaced after ? days		7	1	8-12	12	6
Weight starting sheet, lb	1	13-14	6 91	7 66	6-6½	
Per cent starting sheets used for loops, scrap, etc	12-13		20 27	Loops, 10.85	15	
Deposition tanks:						
Number	15	120	54	576	15	145
Length × width × depth	17-18	330'0" × 4'0" × 4'3"	103' × 2'10" × 3'9"	103" × 2'10" × 3'9"	62'6" × 3'2½" × 4'2½"	62'6" × 3'2½" × 4'2½" × 4'2½"
Number of anodes, cathodes	96, 95	98, 96	25, 24	34, 33	50 × 3	65 × 3
Electric connection		......	Cast-rolled Cu bus-bars	Cast and rolled Cu busbars	3 groups series-electrodes in multiple	
Material of construction			Reinf. concrete lined with 7½-Sb lead	Reinf. concrete lined with 7½-Sb lead		Reinf. concrete mastic-lined asphalt
Circulation, gal/min		100	10	29-44		7.92
Method of leaching	Upward percolation		5 to 6 days countercurrent		Continuous agitation in Pachuca tanks	
Leaching vats:						
Material of construction	Concrete, lead-lined		Reinforced concrete, mastic and acidproof brick lined		7 rows of 4 Pachuca tanks, steel, lead-lined	
Length × width × depth	1750'0" × 676'6" × 1800"		1050'0" × 115'0" × 19'6"		11' diam. × 27'5/16" high	
Average charge per tank, tons	9,000		8,603		5 tons/hr (dry feed)	
Circulation, gal/min	1,800		4 air lifts circulation 2,500 advance 800			
Ore:						
Per cent Cu......	1 087		0.831		Flotation concentrates (oxides) 28	
Per cent Cu, acid soluble	0 527		0 711		Practically 100	
Per cent oxide Cu	0 560		0 120		28 approx.	
Per cent sulfide Cu	Trace				0 2	
Tailings:						
Total per cent Cu	0 148		0 249		0 5-1	
Per cent water-soluble Cu	0 014		0 024		0 5	
Per cent oxide Cu, acid-soluble	0 134		0 126		0 2	
Per cent sulfide Cu			0 099			
Extraction:						
Per cent total Cu	98 385		71 07		97 5	
Per cent oxide Cu	97 343		79 62			
Per cent sulfide Cu	76 071		25 8			

NOTE 1. Two electrical circuits each of 90 tanks in series. Six motor-generator sets: 2 × 4,000 amp 500 volts (1 spare). Five generators of 4,000 amp, 20,000 amp for each circuit.

the ferric sulfate at 7.5 g per liter, between a maximum of 10 and a minimum of 5 g per liter. The consumption of ferric sulfate in the leaching solutions is approximately the theoretical amount required for dissolving the sulfide copper. Inasmuch as the sulfide in the ore dissolves slowly in the ferric sulfate solution at about half the rate of the oxide copper, a dual process was developed. By this method the total iron was carried at about

FIG. 86. General view of leaching plant at Inspiration. (*Engineering and Mining Journal.*)

7 g per liter, and most of the oxide was leached from the ore with about 30 per cent of the sulfide copper. The remaining sulfide was recovered by flotation. Operating details on the plant for both leaching and tank-house sections are given in Table 49.

The electrolytic copper from the tank house runs 99.66 per cent Cu, 0.017 per cent Fe, 0.016 per cent Pb, 0.012 per cent S, and 0.045 oz Ag per ton, with traces of Se, Te, Cl, Zn, Ni, Co, Sn, and Au. At current density of the order of 11 to 12 amp per sq ft (1.2 to 1.3 amp per dm²) cathode efficiencies are about 65 per cent and anode efficiencies of the order of 45 per cent. A general view of the plant at Inspiration is shown in Fig. 86 where the leaching tanks can be seen in the background.

Fig. 87. Excavator and spreader at Inspiration. (*Engineering and Mining Journal.*)
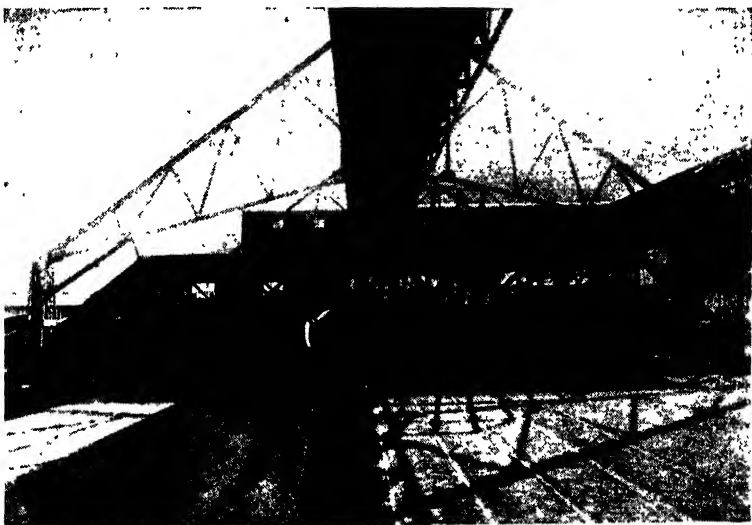
Fig. 88. Ore-reclaiming machine. (*Robins Conveying Belt Company.*)

Handling of large tonnages of low-grade copper ore is feasible only with extensive mechanical equipment. Figure 87 shows one of the excavators and spreaders at Inspiration and Fig. 88 an ore-reclaiming machine of the type commonly used.

Ore Leaching at New Cornelia. At the New Cornelia Mines of the Calumet and Arizona Mining Company at Ajo, Ariz., mixed oxide-sulfide ores were leached by solutions of H_2SO_4 and ferric sulfate. The sulfide-copper minerals consisted chiefly of chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), with small amounts of chalcocite (Cu_2S), while the predominating oxidized-copper mineral was malachite [$CuCO_3 \cdot Cu(OH)_2$] with varying proportions of the oxides and silicates of copper. The ferric iron in the electrolyte was controlled by reduction with SO_2 gas or by the use of cement copper. Starting sheets were manufactured with lead blanks, and the copper in discard solutions was recovered by cementation with scrap iron. The ore showed the following analysis.[7]

	Per cent		Per cent
Cu total..	1.13	Ferric iron.	1.30
Acid soluble	1.00	Ferrous iron...	3 35
Sulfide..	. 0.13	Al_2O_3	15.33
H_2O.....	1.05	CaO and MgO	1.81
SiO_2...	64.40	Na_2O and K_2O. .	5.25
Fe, total.	4.65	S	0 10
	Ag. . .	0.091 oz/ton	
	Au...	0.006 oz/ton	

A typical electrolyte analysis is given in Table 50 and that of the copper produced in Table 51. From 80 to 85 per cent of copper content of the ore was recovered.

TABLE 50. ANALYSIS OF ELECTROLTYE			
	Per cent		Per cent
Cu...................... .	2.64	Cl.....	0.012
Combined H_2SO_4..........	14.23	Al_2O_3...	1.51
Free H_2SO_4.......... . .	1.69	CaO and MgO........	0.85
Total Fe........	1.44	As and Sb.......	0.00
Ferric Fe.......	0.08	Zn and Te..........	Trace

[7] *U.S. Bur. Mines, Circ.* 6303, July, 1930.

TABLE 51. ANALYSIS OF CATHODE COPPER

	Per cent
Cu...... .. .	.... 99.201
H₂SO₄.......	0.312
Cl	0.157
Al₂O₃ and Fe₂O₃. . ..	0.113
Insoluble . . .	0 125
As and Sb.	0 000

Wheeler and Eagle[8] described the development of the leaching operations of the Union Minière du Haut Katanga, where oxidized ores with malachite predominating, with minor amounts of azurite, chrysocolla, cuprite, native copper, and small amounts of sulfides, were treated with leaching solutions of the H_2SO_4 type. The copper mineral was mostly siliceous in character. The nature of the ore was such that it was not amenable to percolation leaching but solution by agitation was employed. The operating details of the plant are given in Table 49.

Callaway and Koepel[9] described the metallurgical plant of the Andes Copper Mining Co. at Potrerillos, Chile, where both sulfide and oxide copper are treated. These, however, are separate, and there is no mixed ore. The oxide ore is treated by leaching with H_2SO_4, which in turn is produced as the result of roasting of sulfide concentrates. Leaching is done in vats with the usual countercurrent washing. The vats are of reinforced concrete and the strong solution produced by leaching runs approximately 41 g per liter Cu, 14 g per liter H_2SO_4, and 7.6 g per liter Fe. The total copper extraction is of the order of 89.7 per cent, while 91.3 per cent of the oxide copper is recovered, giving an over-all figure of 24.57 lb of copper dissolved per ton of ore treated. Operating data on the plant are given in Table 49.

ZINC

The commercial application of hydrometallurgy and the electrolytic deposition of zinc has been of only recent development, being an uphill fight against its strongly intrenched competitor, pyrometallurgy and zinc distillation. The latter method, however, has the severe disadvantages of entailing relatively large losses of metal, fume-handling problems, limitations of equip-

[8] WHEELER, A. E., and EAGLE, H. Y., *Trans. Am. Inst. Mining Met. Engrs.*, **106**, 609 (1933).

[9] CALLAWAY, L. A., and KOEPEL, F. N., *Trans. Am. Inst. Mining Met. Engrs.*, **106**, 678 (1933).

ment as to size, with heavy repair and maintenance charges on the retorts employed, and relatively high necessary labor attendance. For many years zinc electrowinning (involving leaching of roasted ore and ore concentrates, followed by electrolytic deposition of the zinc content of the liquors with insoluble anodes) achieved only slight success and then only in certain localities where conditions were especially favorable. Some of the reasons were that a high power consumption was required to deposit the very base metal—zinc—from an aqueous solution, using an insoluble anode. Difficulties were encountered in obtaining satisfactory cathodic deposits and in finding suitable anode material. In addition the technical details of the production of pure electrolytes of constant definite composition were met, coupled with a lack of market demand for a particularly pure electrolytic zinc. Market demands have changed, especially from the brass industry which is desirous of obtaining high-grade zinc, free from lead and iron. Vast quantities of complex zinc ores were available which were not readily amenable to pyrometallurgical methods but in the treatment of which, leaching processes, coupled with electrolytic deposition, had particular advantages. In addition the subsidiary metals could be completely recovered. The success of copper electrowinning working on low-grade ores offered considerable impetus to the development of a somewhat analogous zinc electrowinning.

Electrolytic zinc plants are now operating on a very large scale in a number of places in the world. In general, the processes employed all involve H_2SO_4 and the production of $ZnSO_4$ electrolytes, which can be divided into those termed low-acid low-c.d., such as employed by the Anaconda Copper Mining Company at their Great Falls and Anaconda, Mont., plants, by the Consolidated Mining and Smelting Company at Trail, B.C., the Hudson Bay Mining and Smelting Co., Ltd., at Flin Flon, Manitoba, Can., and the Electrolytic Zinc Co. of Australasia, Ltd., at Risdon, Tasmania; and the high-acid high-c.d. plants, an example of which is the electrolytic zinc plant of the Sullivan Mining Company near Kellogg, Idaho. An adaptation of the latter has been made in connection with electrogalvanizing where leach liquors are employed as the source of zinc to be applied to articles of iron, particularly wire. The two processes will be discussed in considerable detail with specific examples of each.

Low-acid, Low-current-density Process.[10]   The ores treated at the Great Falls and Anaconda plants are of the complex zinc-lead-copper-iron sulfide type, an example of which is given in the analysis: Zn over 55 per cent, Pb 3 to 4 per cent, Fe 4 to 5 per cent, Cu about 0.5 per cent, and insoluble 3 to 4 per cent. These ores after roasting contain about 60 per cent Zn (92 to 95 per cent of which is acid soluble) and about 3 per cent S, of which only 0.1 to 0.2 per cent is in the form of sulfide, the balance of the sulfur being in the form of sulfates.

In the roasting of concentrate containing 5 per cent iron or less, almost all the iron combines with zinc as $ZnO \cdot Fe_2O_3$, which is nearly insoluble in dilute H_2SO_4. As the iron content increases above 5 per cent, the combination of zinc and iron oxides can be partly controlled by careful regulation of temperatures on the various hearths of the roasting furnaces. The total sulfur content of the calcine produced is regulated by the acid requirements of the plant, sulfide-sulfur content being kept at all times at 0.2 per cent or less. Acid losses are small, being chiefly as lead sulfate, basic iron sulfate, and entrained zinc sulfate in the residues discarded from the plant.

The roasting furnaces are operated to convert the zinc sulfide in the ore to acid-soluble oxides and sulfates and at the same time produce SO_2 which is used for the manufacture of H_2SO_4 employed in leaching.

Ore Leaching.   The flow sheet of the plant is given in Fig. 89. In general the procedure is cyclic. Electrolyte from the cells, after the greater portion of the zinc content has been deposited, is used to leach untreated roasted ore, termed "calcine," the solids and liquids being separated and the zinc-sulfate solution being purified by means of metallic zinc. Another portion of spent electrolyte is employed for a second leach of the resultant sands from the first treatment of ore by spent electrolyte, while still a third portion of the electrolyte is used to leach the residue from the second leaching, the resultant solutions traveling back to join the main bulk of the electrolyte in the original or neutral leach. Spent electrolyte from the solutions contains 10 to 11.5 per cent H_2SO_4 and about 2.5 per cent zinc. After the leaching

[10] LAIST, F., FRICK, F. F., ELTON, J. O., and CAPLES, R. B., *Trans. Am. Inst. Mining Met. Engrs.*, **64**, 699 (1921); WIGGIN, A. E., and CAPLES, R. B., *Eng. Mining J.*, **128**, 319 (1929).

treatment the liquor runs about 0.5 per cent H_2SO_4 and 10 per cent zinc.

Actual leaching operation is divided into three steps: (1) neutral or purification leach; (2) acid or finishing leach; and (3) retreatment of residue from (2).

The first two leaching steps are continuous operations carried on in unlined Pachuca[11] tanks using compressed air for agitation.
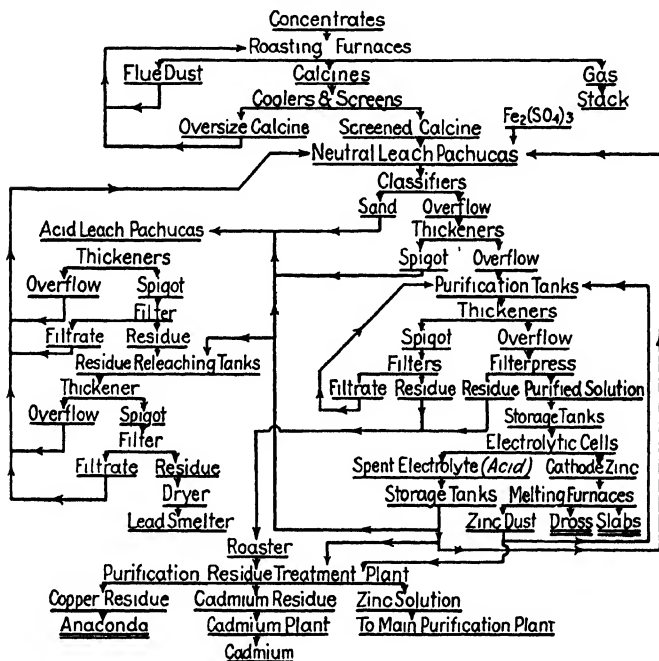
FIG. 89.   Flow sheet of the Great Falls plant.

Residue leaching is a batch operation conducted in mechanically agitated wooden tanks.   No lead-lined tanks are used for leaching, and no outside heat is supplied for leaching in the first and second steps.   Solution going into the residue releaching operation is heated before adding the residue.   Elevators equipped with bronze buckets are used for elevating pulp.

As less than 5 per cent of the iron contained in the calcine is soluble in the acid strength employed in the first and second

[11] A vertical, cylindrical, cone-bottomed tank provided with an air lift for agitating and aerating purposes.

leaching steps, scrap iron is dissolved in spent electrolyte and the resulting ferrous-sulfate solution is oxidized to ferric sulfate by MnO_2 and is added to the first, or neutral, leach step, as required for purification of solution for arsenic and antimony.

To the neutral leach is added all the calcine but only a part of the acid (spent electrolyte), resulting in the presence of an excess of zinc oxide for precipitation of such impurities as iron, silica, alumina, arsenic, and antimony. The pulp from this leach goes to classifiers and thickeners, the thickener overflow going to purification tanks and the spigot product to the second, or acid, leach. Classifier sand goes to the acid leach tanks.

Spent electrolyte is added to the second, or acid, leach in sufficient quantity to dissolve all uncombined zinc oxide in the residue from the first, or neutral, leach and to ensure an excess of acid in the leach discharge, excess acid being provided to ensure complete solution of free zinc oxide. The discharge from this leach goes to acid thickeners, the overflow being returned to the first or neutral leach and the spigot product delivered to filters.

The undried filter cake is sent to mechanically agitated leaching tanks previously filled with hot, spent electrolyte. As the leach progresses, part of the zinc-iron compound is decomposed giving a solution rich in ferric sulfate and lowered in free acid. A further reaction between the ferric sulfate solution and zinc ferrite results in solution of the zinc oxide and precipitation of the iron as basic sulfate. While still acid, this leach is discharged to thickeners, the overflow going to the first, or neutral, leach and the spigot to a Moore filter, where the residue is washed nearly free of entrained zinc sulfate solution. The pulp resulting from the Moore filter operation goes to Oliver filters for dewatering, and the Oliver cake goes to driers for partial drying before shipping to a lead smelter for the recovery of lead, silver, gold, and copper.

Residue from the final filters contains 35 to 40 per cent moisture and is dried to about 15 per cent before shipment to the lead smelter.

To sum up, in the first or neutral leach: (1) All the calcine enters the process, and approximately three-quarters of the soluble zinc is taken into solution. (2) The iron is oxidized and precipitated. (3) Gelatinous silica is coagulated by excess base

and rendered granular. (4) The arsenic and antimony are completely precipitated. (5) Eighty per cent of the copper is precipitated as hydroxide by the excess base. This makes possible the cheap removal of most of the copper and supplies the iron for the removal of arsenic and antimony in the acid leach. (6) A large percentage of the zinc is separated from the residue and is contained in a clear settler overflow (along with 20 per cent of the soluble copper and all the soluble cadmium) which goes to the purification plant. The settler spigot product containing 3 parts of solids and 2 parts of solution is elevated to the acid leach. The only heat used in the process is that supplied by the chemical reactions and electric current in the tank room.

The results of the acid-leaching system are: (1) solution of the remainder of the acid-soluble zinc and the copper, (2) final separation of the solids from the zinc and copper solutions, (3) roughing out of the copper and chlorine, (4) solution of sufficient iron to guarantee the removal of arsenic and antimony in the neutral leach step, (5) elimination of the arsenic and antimony which are only partly redissolved in dilute acid. About 10 per cent of the arsenic and antimony circulate in the acid thickener overflow.

Metal Precipitation by Electrolysis. Successful electrolytic deposition of zinc from a sulfate solution depends primarily upon the purity of the solution fed to the cells. Every effort is made in the leaching and purification plants to produce a solution entirely free from metals more noble than zinc. Materials of construction are carefully selected to avoid contamination. The effect of a number of impurities on the electrodeposition of zinc from a sulfate solution has been carefully studied. While fairly accurate limits have been established for single impurities, comparatively little is known regarding the combined effect of these impurities in varying proportions. With pure solutions and noncontaminating materials in contact with the solution, high current efficiency is consistently obtained; but with either impure solution or contaminating materials the results are erratic. Therefore the highest possible standard of purity is maintained.

The Great Falls electrolyzing division is divided into eight electrical circuits of 144 cells each, arranged in cascades of 6 cells each. Current from a rotary converter at 580 volts supplies each circuit, or unit. The general data on this plant are given in Table 52.

Spacing of electrodes is 3 in. center to center of anodes. Current density is 30 amp per sq ft (3.2 amp per dm^2) of cathode area.

The solution is distributed from storage tanks through lead pipe lines to individual cascades of cells and is taken from header lines through iron pipes to the individual cells. Flow to each cell is so regulated as to maintain a practically constant acid and zinc concentration in each cell. The electrical resistance of the electrolyte is taken to determine the acid strength, readings so obtained being occasionally checked against a standard chemical method. The feed to the cells averages approximately 110 g of zinc per liter, while the cell discharge averages about 105 g of H_2SO_4 per liter. Spent electrolyte is collected by a system of launders[12] and delivered to storage tanks, from which solution is drawn as needed for the leaching plant and purification residue re-treatment plant.

The cells are cooled by circulating water through a lead coil placed in each cell. Cell temperatures vary from 37 to 41°C, depending upon atmospheric and cooling-water temperatures. From 8,000 to 15,000 gal of water per ton of cathodes produced is used for cooling purposes.

Effect of Electrolyte Impurities. The effect of metallic impurities in practice has been summed up by Laist.[13] Antimony is most harmful and even when 1 mg per liter is present in the electrolyte, sprouts develop on the cathode and current efficiency is lowered. The electrolyte should be so free from antimony that the element is not detectable. Arsenic and cobalt are nearly as dangerous in that 1 mg per liter of arsenic causes rough deposits. As little as 1 mg per liter of cobalt produces corrosion holes in the deposited zinc, and when larger amounts of cobalt are present, honeycombing develops. Copper up to 10 mg per liter has little effect. Larger amounts aid the formation of zinc holes and cathodic corrosion, as well as intensify the bad effect of any antimony or arsenic. The deposition of iron impurities is retarded, but the presence of iron in quantities greater than 20 to 30 mg per liter decreases the current efficiency due to the alternate oxidation of ferrous and the reduction of ferric ions. Lead is probably not harmful at the concentrations reached in $ZnSO_4$

[12] An open trough or channel.
[13] Laist, Frick, Elton, and Caples, *loc. cit.*

TABLE 52. ELECTROWINNING OF ZINC

	Anaconda Copper Mining Company, Great Falls, Mont.	Consolidated Mining and Smelting Co., Trail, B.C.	Electrolytic Zinc Co. of Australasia, Ltd., Risdon, Tasmania	Hudson Bay Mining and Smelting Co. Ltd., Flin Flon, Manitoba	Sullivan Mining Company, Kellogg, Idaho	American Smelting and Refining Co., Corpus Christi, Tex.	American Zinc Company of Illinois, Monsanto, Ill.
Electrolyte:							
Sp gr	1 25-1 30	Sulfide 1.332	1 33	1 33	1 35		1.33
Concentration Zn to cell, g/l	110-120	Oxide 147, sulfide 138	110	32	215	172	135
Concentration Zn from cell, g/l	45	Oxide 62, sulfide 55	46 (approx.)	54		56	50
H₂SO₄, cell discharge, g/l.	100-110	Oxide 114, sulfide 112	100	115	22-27%	200	115
Temperature, °C	40	36	35	23-35 (av. 27.6)	30-35	36	38-40
Feed to cells	Cascade and individual	Cascade and individual	Cascade and individual	Cascade and individual	Batches (variable)	Cascade and individual	Cascade and individual
Circulation, gal/min	6	...	None but feed rate 1.20 gal/min	0.35 per cell	10	10	0.57 per cell
Current:							
Amp/sq ft.	30	42	30 (cathode)	38 6	100	60	31
Voltage	3 7	3 7	3.55 (includes bus-bar loss)	3 57	3 4	3	3 25
Current efficiency, %	90	Oxide 90, sulfide 93	92-93	93 1	88-93	94 7	88-90
Current kw per generator	5,500	See note 1	See note 2	7 motor generators each 3,680 kw. 6,400 amp, 575 volts	6 motor generators, each 4,000 amp, at 500 volts	2 circuits, 5-2,500 kw 10,800 amp	See note 5
Kwhr/lb zinc	1 6	A.c. 1.59	1 57	1.63 a c-1 47 d.c.	1 55	1 48	1.404
Anode:							
Composition	Lead	Ag-Pb alloy (0.75% Ag)	See note 3	Ag-Pb alloy (1% Ag)	Lead alloy	Ag-Pb alloy	Ag-Pb alloy
Length, width, thickness	45" × 24½" × 3/16"	9.2 sq ft submerged × 1/8"	45⅜" × 28" × ⅜"	40?" × 28" × 5/16"	32" × 21" × 3/16"	31" × 19⅝" × 5/16" grid	23½" × 40½" × ¼"
Weight, lb	103	100	176	135			60
Mode of suspension	Cast around copper header	Welded to busbar	Cast around conductor (copper) 10-ton unit	Cast around conductor	Cast around conductor	Welded to bar cast around conductor	Lead cast around conductor
Anode spacing, in.	3	3	3.5", rest 3"	3½	1¾	3	3
Construction	Solid, cast	Solid	Solid	Solid	50% perforated	Grid	Rolled punched sheet
Life, years	Recast after 3 months	4+	2 5-3	3+			3

TABLE 52. ELECTROWINNING OF ZINC.—(*Continued*)

	Anaconda Copper Mining Company, Great Falls, Mont.	Consolidated Mining and Smelting Co., Trail, B.C.	Electrolytic Zinc Co. of Australasia, Ltd., Risdon, Tasmania	Hudson Bay Mining and Smelting Co. Ltd., Flin Flon, Manitoba	Sullivan Mining Company, Kellogg, Idaho	American Smelting and Refining Co., Corpus Christi, Tex.	American Zinc Company of Illinois, Monsanto, Ill.
Cathode:							
Composition	Aluminum	Aluminum sheet	Rolled aluminum sheet	Aluminum sheet	Aluminum plates	Rolled aluminum sheet	2 S aluminum
Starting sheet, length, width, thickness	45" × 24" × 3/16"	9.4 sq ft submerged × 3/32"	45" × 25" × 1/4"	31" × 24" × 1/8" immersed	Immersed 27" × 21"	36" × 21" × 3/16"	40½" × 24" × 7/32"
Life, years		1+	2-3	31 months			2
Mode of suspension	Riveted to copper header	Riveted to conductor	2 riveted Cu bars	Welded to Al conductor with Cu inser- at busbar contact	Lead-covered wood frames	Welded to Al conductor	Welded to conductor
Removed after ? hr.	24	24	72	24	8-12	24	24
Weight, lb	2 sheets, each 11	2 sheets, each 12	45 (including head bars) 28 (excluding head bars)	2 sheets, each 13		... .	2 sheets, each 11
Deposition tanks:							
Number	1,248	1,170 tanks, 2 cells each	4 units each 144, 1 unit 72 See note 4	840	450	320	372
Length, width, depth	103" × 19" × 2'10"	60" × 7'6" × 4'10"		7'3" × 2'10" × 3'8"	6'3" × 2'6" × 3'9"	7' × 2'6" × 4'6"	8' × 4'10" × 2'10"
Number anodes, cathodes	33, 32	24, 23	4 units 45, 44; 1 unit 28, 27	18, 17	24, 12	25, 24	28, 27
Materials of construction	Concrete, lead-lined	Concrete, rubber-lined; or "Prodorite" tanks	Wood, lead-lined	Prodorite	Wood, lead-lined	Concrete, lead-lined	Reinforced concrete, lead-lined
Tank mud:							
Composition	MnO₂	MnO₂	MnO₂, Zn 4.3%, Mn 39.8%, 3.55%	MnO₂ and gyp... (4 to 15% Mn)	MnO₂	...	MnO₂
Amount	2 lb/ton of feed	Mn 40%, Pb 8%	1.5 g/l	0 5 lb/ton feed	.		Variable
Removed after ? weeks	13	4	4-5	4	4		5½

1. Thirteen motor-generator sets = 26 generators, 4,000 amp each at 125 volts
   Ten rotary converters, 4,500 amp each at 550 volts.
   Three mercury-arc rectifiers, 9,000 to 10,000 amp at 560 volts.
   One mercury-arc rectifier, 10,000 amp at 670 volts.
2. Units 1, 2, 3 three rotary converters in parallel. 18,000 amp, 510-520 volts
   No. 4 unit shut down. 10-ton unit 2 motor-generator sets in parallel.
   10,000 amp at 250 volts.
3. 10-ton unit 1% Ag Pb. Remainder 0.01% Ag Pb.
4. Four units 12'10½" × 2'9½" × 4'6½".
   One unit 103" × 2'9½" × 4'10".
5. Two 3,000 kw. 5,000 amp, 600 volts.
   Mercury-arc rectifiers, two 10,000 amp, 710 volts.

solutions, and cadmium does not affect the character of the deposit unless present in concentrations greater than 500 mg per liter; but for the production of cadmium-free zinc the concentration should be below 50 mg per liter. By itself manganese is not harmful but appears to emphasize the bad effect of other impurities. It is deposited as MnO_2 on the anode and its concentration in the electrolyte is best kept below 350 mg per liter. Metals more noble than zinc must be absent to allow the production of good cathodic deposits. The effect of impurities is given in Table 53.

Tainton and Clayton[14] found that in the electrolysis of zinc sulfate solutions derived from the leaching of roasted Joplin concentrate, violent fluctuations of current efficiency occurred, zinc deposits showed a great tendency to redissolve, and sometimes no zinc was deposited at all. The ordinary impurities such as antimony, cobalt, nickel, and arsenic, which are known to produce such effects, had been removed so that the influence of some other element in the solution was suspected. This proved to be germanium, which is found to cause serious loss in efficiency at concentrations as low as 1 mg per liter. Experiments showed that treatment of the solution with precipitated ferric hydroxide removed the germanium. Normally the ores contain sufficient iron to prevent this element from entering the solution, but some of the Joplin ores are very low in iron and apparently high in germanium. The trouble was remedied by starting with a mixture of concentrates containing a sufficient total proportion of iron to effect complete removal of germanium.

Combination Leaching. At the Trail plant of the Consolidated Mining and Smelting Co., treatment of complex zinc concentrates involves suspension roasting, leaching and purification, electrolysis, melting, and cadmium recovery.[15] This is referred to as the "sulfide leaching." Another portion of the plant, termed the "oxide leaching section," treats zinc fume obtained from slag-fuming operations at the lead smelter. The purified leach liquors from both the sulfide and oxide plants become the electrolyte for the tank room. Operating data are given in Table 52.

[14] TAINTON, U. C., and CLAYTON, E. T., *Trans. Am. Electrochem. Soc.*, **57**, 279 (1930); *Chemistry and Industry* (London), **49**, 718 (1930).

[15] HUTTL, J. B., *Eng. Mining J.*, **139** (9), 42 (1938).

TABLE 53. IMPURITIES IN ZINC ELECTROLYTES

		Effect on current efficiency	Action on cathode deposit	Normal concn., mg/l	Max. allowable concn., mg/l	Remedy
Antimony	Most injurious	Lowers	Spongy and dark	1	Less than 0.5	Better purification, lower temperature, shorter deposition
Arsenic	. .	.	Corrugations appear, low luster	....	Less than 1	Purification
Cobalt	Most serious, difficult to remove	Lowers	Re-solution at 10 mg/l	....	1	Cobalt lowers Pb in deposit
Germanium	Detrimental when with Co	....	. . . . . .	0.01	0.001	Requires special removal methods when present
Nickel	Most serious, difficult to remove	Lowers	Re-solution at 0.5 mg/l	0.01	0.01	
Copper Cadmium	. . . .	No effect No effect	Contaminates	10 500	Below 10 50	For cadmium free Zn, Cd must be below 50 mg/l
Lead	Plates out with zinc	No effect	. . . .	Solubility of PbSO$_4$ in electrolyte	...	
Iron Manganese	..	Lowers No effect	Deposits as MnO$_2$ at anode	20 to 40 3,000	Less than 20 350	Large amounts cause holes in Zn deposit. Better purification by oxidation
Chlorine	Increases corrosion of Pb anodes	None	Excess of Cl- causes adherence of Zn to starting sheets	100	Less than 50	Reduce concentration by precipitation
Fluorine	Increases corrosion of Pb anodes	None	Causes sticking and corrosion of cathode sheet	......	....	Eliminate in roasting process. No commercial removal method
(NO$_3$)-	Increases corrosion of Pb anodes	None	Causes higher Pb content			Discard portion of electrolyte at intervals
Sodium, potassium Calcium	Harmless Harmless	None None	None None	Solution limit of CaSO$_4$ in electrolyte		
Aluminum Magnesium	Harmless Harmless	None None	None None	.	Solution of Mg complex sulfates	

Carr and Reikie[16] have described the Flin Flon plant of the Hudson Bay Mining and Smelting Company, Ltd., which uses the low-density method where the zinc is carried through the plant solution circuit in the form of a sulfate at a concentration not exceeding 175 g per liter of zinc. The leaching plant operates in such a manner that there is a neutral leach, purification, an acid leach, and cadmium concentration. In the tank room anode-cathode spacing is maintained by the use of threaded lead studs inserted near the bottom of each lower corner of each anode, to which studs, porcelain buttons similar to door knobs, are screwed on both sides. The cathodes are held in place between the buttons of adjacent anodes. Purer zinc is produced as the result of the decrease of the transfer of lead from the anodes to the cathodes, as well as the maintenance of better alignment. Lead-alloy and silver-lead anodes are used. Operating data for the plant are given in Table 52.

High-acid, High-current-density Process.[17] The electrolytic zinc plant of the Sullivan Mining Company located near Kellogg, Idaho, was erected to treat the zinc-bearing ores of the Coeur d'Alene district. These ores cannot be classed as particularly favorable for electrolytic treatment, inasmuch as they tend to form an unusually large amount of insoluble zinc ferrite in the roast and yield appreciable quantities of gelatinous silica in the leaching operation. Furthermore, they contain relatively large amounts of cobalt, which is one of the most troublesome impurities from the standpoint of electrolytic zinc treatment. This plant employs the Tainton high-acid process, in which the return electrolyte used for leaching carries 28 to 30 per cent free acid, and the electrolysis is carried out at a current density of 100 amp per sq ft (10 amp per dm²), both of these amounts being about three times as great as the corresponding figures in ordinary electrolytic zinc practice.

The American Smelting and Refining Company plant at Corpus Christi, Tex., has been described by Cunningham and

[16] Carr, J. D., and Reikie, M. K. T., *Can. Inst. Mining Met.*, 1935, p. 287.

[17] Tainton, U. C., and Leyson, L. T., *Trans. Am. Inst. Mining Met. Engrs.*, **70**, 486 (1924); Tainton, U. C., and Clayton, E. T., *Trans. Am. Electrochem. Soc.*, **57**, 279 (1930); Tainton, U. C., and Bosqui, D., *ibid.*, **57**, 241 (1930).

Jephson.[18] This might be described as a high-acid (200 g H_2SO_4 per liter), high-zinc-content (172 g per liter) electrolyte operated at an intermediate current density of 60 amp per sq ft as compared to the Sullivan use of 100 amp per sq ft. Cell drops are of the order of 3 volts at 10,800 amp per cell. Operating data for this plant are given in Table 52.

Davidson[19] described the plant of the American Zinc Company of Illinois at Monsanto, Ill. Operating data are given in Table 52.

Ore Roasting and Leaching. An important difference between the leaching processes employed at Great Falls, Anaconda, and Trail and that employed at the Sullivan plant is found in the method of treating the ore during roasting. At first glance the fundamental reactions involved in the leaching of zinc ores appear to be simple. Zinc sulfide may be completely oxidized without difficulty. Zinc oxide is totally soluble in H_2SO_4, even in hot $ZnSO_4$ solution. In practice, however, unaccountable difficulties appeared in the first plants in obtaining complete solution of the zinc and in separating the solution from the residue. Investigation proved that during the roast, ferric oxide and zinc oxide combined to some extent to form zinc ferrite, $ZnO \cdot Fe_2O_3$, insoluble in dilute acids. Furthermore, treatment of a roasted zinc ore with acid will dissolve a certain quantity of the iron and silica content. When the acid is later neutralized by continued addition of roasted ore, the iron and silica are precipitated in the form of hydrated ferric oxide and gelatinous silica. These substances will markedly lower the filtration rate and may even make it impossible to separate the solution from the ore. As a result, the residues from the modern electrolytic zinc plant ordinarily carry 12 to 20 per cent of zinc, the average being nearer the higher figure.

It has been previously pointed out that solutions as pure as possible are necessary for electrolytes. The increasing complexity of the flow sheet of a modern electrolytic plant emphasizes the importance of obtaining pure electrolytes on the one hand and at the same time obtaining a high extraction of zinc from

[18] CUNNINGHAM, GEORGE H., and JEPHSON, ALLEN C., *Trans. Am. Inst. Mining Met. Engrs.*, **159**, 194–209 (1944).

[19] DAVIDSON, L. P., *Trans. Am. Inst. Mining Met. Engrs.*, **159**, 189–93 (1944).

the ores.   If the residue going out of the plant has been treated with a solvent sufficiently active to make a high extraction of the zinc values, other constituents of the ore must also have been taken into solution and must be eliminated before the solution can be used for electrolysis.

The double-leaching method as practiced at Great Falls is one way out of the difficulty.   The residues going out of the plant are finished in acid solution.   By separating this solution and neutralizing it with an excess of roasted ore, many other constituents are precipitated.   This basic solution is then separated and goes forward to precipitation.   The solids, containing an excess of calcine, are treated with the acid solution before going out of the plant.

Although effective in extracting zinc oxide, the double-treatment system cannot be employed to break up zinc ferrite. Effort at the zinc plant has therefore been centered upon obtaining as much of the zinc as possible in oxide form.   The most effective method, and the one which has been generally adopted, is to keep iron out of the zinc concentrate.

In the Tainton process, zinc ferrite is separated magnetically from the calcine, and in the leaching process is first added to a strongly acid solution resulting from stripping the electrolyte in the deposition cells, the neutralization of the acid being then completed by the use of the zinc oxide portion of the calcine, free from ferrite.   With the allowable production of zinc ferrite in the calcine, less close control on roasting is necessary than is needed for the usual type of leaching of zinc ores.

By the use of high-acid concentration, Tainton claims the following advantages:

1. It permits the treatment of zinc ferrite, which is ordinarily an obstacle in the treatment of low-grade ferruginous concentrates, and enables the roasters to be operated at high capacity.

2. It increases the percentage extraction of both zinc and copper, and reduces the amount of zinc in the residues, thereby lowering residue smelting costs.

3. It brings about the solution (and subsequent precipitation) of a large quantity of iron in the leach, and thus thoroughly purifies the solution from arsenic and antimony.

4. It improves filtration and permits the treatment of ores high in soluble silicates which, in low-acid work, would give trouble in filtration from gelatinous silica.

5. It allows the treatment of ores containing large quantities of cobalt or nickel without the addition of any extra step in the flow sheet.

6. It reduces the quantity of pulp to be agitated and filtered, and the volume of solution to be stored and purified.

In starting a charge, return electrolyte which has been heated to 60°C is pumped into an agitator tank. A charge of ferrite is then put in, a quantity of MnO_2 added to oxidize the iron, and the tank allowed to agitate for 1 hr to decompose the zinc ferrite. The feeder of the oxide bin is then started and addition continued until all the iron is precipitated, as shown by a test with thiocyanate spot paper. Before the reaction is completed, the pulp reaches boiling temperature, with the evaporation of an appreciable quantity of water. Stacks are provided to take care of the steam evolved. When the charge is neutralized, the pulp is dropped into a storage tank of the same size as the agitators, from which it feeds to filters. A charge of pulp is dropped into a filter, the solution separated, and the cake washed with water, after which the residue is repulped in the filter and sent to a thickener. From this thickener the residue feeds to a filter and thence to a drier, which reduces the moisture to a point where the residue is easily handled for shipment. Overflow from the thickener is not used as wash water but is returned for repulping a fresh charge. The washing in the filter is so complete that the amount of soluble zinc in the repulping water is unimportant. Figure 90 shows the filter-press section for electrolyte purification.

Solution from the filters goes into the purification system to eliminate copper, cadmium, and cobalt. This is done in mechanical agitator tanks 22 ft in diameter and 12 ft deep, holding enough solution for the production of 28 tons of zinc at a single charge. The solution is agitated with zinc dust at a temperature of 80°C. The metals are completely precipitated, so that the purified solution usually contains less than 5 mg per liter of cadmium and copper and less than 2 mg of cobalt. After precipitation of the metals, the residue is passed by means of centrifugal pumps through filter presses. After filtration the solution goes to storage tanks known as "check tanks," each of 250 tons capacity. Each lot of solution is checked by the laboratory before being pumped over to the neutral storage tanks, whence it feeds to the cell circuit. Great care is taken to avoid introducing

an impure solution into the electrolytic circuit where it would lower the grade of zinc produced and possibly give trouble in electrolysis.

Electrolytic Plant. In the electrolytic division there are two circuits, each of 4,000-kw capacity and each supplied by a motor-generator set giving 8,000 amp at 500 volts on the d.c. side. There are 150 cells in a circuit, each taking 8,000 amp. Each cell contains 10 cathodes having a submerged area of 4 sq ft on each side and taking 800 amp in normal operation. The

Fig. 90. Filter presses handling purified pulp solution from tanks. (*Engineering and Mining Journal.*)

cathodes are of commercial aluminum sheet having an aluminum conductor bar welded at the upper end. Current is led into the conductor bar through a spring clip at the side of the cell, the end of the bar being copper-plated to provide good contact. This type of construction has proved superior to that previously used with a copper bar riveted to the aluminum plate.

The cathodes slide in grooved wooden guides fixed in the cell with a wooden framework. The framework also holds the anodes in fixed position and at a definite spacing from the cathode face. Two anodes are placed between each two cathodes, the anodes being perforated below the solution line to permit free circulation of the electrolyte, to reduce the terminal voltage, and

to lessen the acid spray in the air. During operation solution is circulated to all cells in parallel from a feed launder directly over the center of each cell. The solution passes through a hard-rubber pipe to the center of the cell, overflowing through hard-rubber pipes at each end to a sump below. From here it flows through a thickener for the recovery of MnO_2, the overflow passing to a storage tank termed the "balance tank," which is used to keep the circuit in balance when adding or withdrawing solution.

Fig. 91. Electrolyte cooling system of lead coils. (*Engineering and Mining Journal.*)

From this tank hard-lead pumps send the solution through a system of cooling coils and back to the electrolytic cells. Figure 91 shows banks of lead cooling coils around which the electrolyte circulates for cooling to the working temperature of the electrolytic cells. The speed of circulation is so regulated that the entire volume of solution passes around the circuit once every hour and a half, thus maintaining uniform composition in the cells and constant conditions for electrolysis.

Solution enters the cell circuit in batches about once every 24 hr. This reduces the acid strength in the circuit from about 28 to 22 per cent, which is the normal range of electrolysis. When the acid has risen to the proper point, a batch is withdrawn from the circuit and pumped up to the acid storage tanks. A corresponding quantity of neutral solution is then dropped in order to bring the volume of the circuit up to normal.

Manganese dioxide precipitated during electrolysis is pumped as a sludge from the manganese thickener, filtered, washed, and prepared for market.

An interesting problem arose in the electrolytic division regarding the best type of cooling system. Deposits formed on any cold surface that was used for cooling purposes and were mechanically removed at intervals. In the present plant the cooling system consists of several long boxes 4 ft square down which the solution flows. Flat lead coils are set transversely across these boxes, carrying cool water in the direction opposite to the solution flow. To prevent the formation of deposits on these coils, lead grids are placed between the coils, provision being made to connect the entire system in series with the cell circuit, so that 8,000 amp can be passed through the solution from the grids to the coils, the coils being the cathodes. This operation, performed at short intervals, plates a thin film of zinc on the coils. As the coating dissolves, hydrogen is evolved and any scale adhering to the coil is broken away. The efficiency of the cooling system is thus maintained at its maximum.

In general, the low-acid low-c.d. process shows higher current efficiency than does the high-acid high-c.d. By far the greater portion of electrolytic zinc is produced by the former method. Manganese dioxide and cadmium are by-products of both processes. Comparative operating data on two low-acid low-c.d. and two high-acid, high-c.d. plants are given in Table 52. Figure 92 shows a row of electrolytic zinc cells at the Sullivan refinery.

CADMIUM

Cadmium is found in very small quantities in most ores. It can be profitably produced only as a by-product in the manufacture of some other metal. An important source of raw material is the baghouse condensation products from lead and copper furnaces, from which cadmium can be recovered electrolytically. Zinc ores and blue powder constitute another source of the metal through fractional distillation. .

At the Kennett, Calif., plant of the United States Smelting, Refining and Mining Company,[20] the raw material was a baghouse condensation product from copper furnaces running 0.55 per cent cadmium, 19 per cent zinc, 6.6 per cent arsenic, with

[20] HANLEY, H. R., *Chem. & Met. Eng.*, **23**, 1257 (1920).

appreciable amounts of Te, Se, Co, Ni, Tl, and of the more commercial metals such as Cu, Au, Ag, Bi, and Pb. This raw material was treated for the recovery of zinc by the electrolysis of a sulfate solution. A H_2SO_4 leach gave a solution of the following composition: Zn 96.0 g per liter, Cu 8.0 g per liter,

Fɪɢ. 92. A row of electrolytic zinc cells. (*Engineering and Mining Journal.*)

Cd 5.0 g per liter, Fe 2.0 g per liter, Mn 0.04 g per liter, As 0.5 g per liter, Bi trace, Co 0.015 g per liter, Ni 0.012 g per liter, Tl trace, Te trace.

In zinc recovery the solution was treated with powdered lime rock and agitated by air. This precipitated the iron and traces of arsenic, and removed about 40 per cent of the copper but none of the cadmium. The resulting solution contained approximately equal quantities of cadmium and copper. These were

precipitated by zinc dust, forming a black mud containing approximately 25 per cent copper, 25 per cent cadmium, and 30 per cent zinc—the raw material for cadmium production.

The cadmium was recovered from the wet cadmium-copper-zinc precipitate. The wet mud was leached with H_2SO_4 solutions to dissolve out cadmium and zinc, and the cadmium precipitated out of solution by sheet zinc. The precipitated cadmium was then washed and dissolved in an acid electrolyte, in which form it passed to the system for purification and iron removal before going to the deposition cells. Iron was removed by the use of hydrated lime and air, the sludge formed being filtered off. The solution, if low in thallium, was delivered to the feed tank supplying the electrolytic cells. When thallium had accumulated to a certain amount, the solution was treated for its removal.

Considerable attention has been given to the electrodeposition of cadmium, efforts centering especially upon preventing the formation of trees, sponge, and the like upon stationary cathodes. Neutral solutions will yield not a metallic deposit but a spongy mass which is melted only with great difficulty. A coherent deposit may be obtained from acid solutions, but the troublesome trees and sprouts are also produced in quantity. Agitation of the solution does not improve the quality of the deposit. It has been found, however, that from acid solutions rotating cathodes will produce a smooth metallic cadmium, comparatively free from irregularities.

Rotating Cathode Cells. Electrolysis in the Kennett plant was carried on in two of three semicircular cells lined with lead. The circular anodes—segments of considerably less than a half circle—were supported upon double-grooved porcelain blocks laid upon the lining of the cell. The anode was entirely submerged in the electrolyte, only that section protruding which connected with the copper bars, these in turn connecting with the anode bus. There were two anodes for each cathode throughout the cell, the anodes being 2 in. less in radius than the immersed portion of the cathode.

At the plant of the Electrolytic Zinc Co. of Australasia, Ltd., where cadmium is recovered from a zinc-dust precipitate from zinc electrolyte purification, rotating cathode cells are employed of the type shown in Fig. 93. Operating data of the plant are given in Table 54.

Cadmium Recovery from Zinc Electrolyte Residues. Stationary cathodes are used in most cadmium plants. The raw material is the cadmium residues from the electrolytic zinc process. The treatment of this raw material at the Anaconda plant has been described by Mitchell.[21]

Cadmium that is dissolved during the leaching operation in the zinc process is precipitated with metallic zinc, ordinarily added
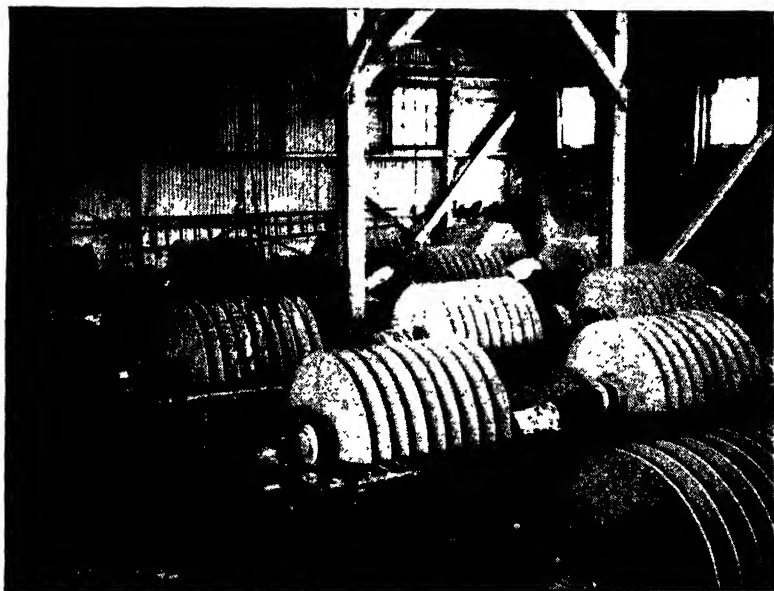
Fig. 93. Electrolytic cells for the production of cadmium. (*Electrolytic Zinc Co. of Australasia, Ltd.*)

as zinc dust. Any copper which has been taken into solution will come down at the same time, so that the precipitate will consist of cadmium, copper, and zinc which has been added in excess to ensure complete reaction. The mass is roasted at 700°C in gas-fired McDougall furnaces to render insoluble the iron, arsenic, and antimony impurities and at the same time increase the solubility of the metals to be recovered. The roasted residue is leached with agitation in cylindrical tanks of 30 tons capacity, the solution being spent electrolyte from the zinc process containing 10 to 12 per cent H_2SO_4. The leaches are finished neutral and decanted to thickeners. The thickened residue, low

[21] MITCHELL, W. E., *Trans. Am. Inst. Mining Met. Engrs.*, 239 (1930).

in cadmium and zinc but with an appreciable amount of copper, is filtered and washed, dewatered, dried, and shipped to a copper smelter. The overflow from the thickener, containing all three metals, is treated for the removal of copper by careful addition of zinc dust, the operation being carried out in large tanks with mechanical agitation. The resultant high copper residue is separated from the solution in a thickener, filtered, and shipped to a copper smelter. In like manner the cadmium is precipitated in a finely divided state from the remaining solution by addition of zinc dust. The slight excess of zinc necessary for complete precipitation constitutes an impurity in the cadmium. The cadmium sponge is separated from the solution by filtration.

The cadmium sponge dissolves very slowly in dilute H_2SO_4 but more rapidly if the sponge be oxidized. It is therefore piled in deep heaps while wet as produced, and allowed to oxidize over a 2- or 3-week period. Partly oxidized sponge is then leached with spent electrolyte from the electrolytic cadmium cells, carried to the neutral point, and settled in the leach tanks. The clear solution is filtered through a filter press, then pumped to a storage tank from which it flows by gravity to the electrolytic cells. The residue is left in the leach tank until it has accumulated in sufficient quantity to require a cleanup. This residue and the mud from the filter press are returned to the plant treating the regular zinc dust purification precipitate.

The advantage in using partly oxidized sponge is that it contains sufficient metallic zinc and cadmium to give a good purification. If the sponge be too high in copper or has become completely oxidized, the solution may run high in copper, necessitating the addition of small quantities of freshly precipitated sponge to bring down the dissolved copper.

Although rotating cathodes are frequently used to overcome the treeing tendency, the Anaconda plant at Great Falls obtains satisfactory cadmium deposits with stationary cathodes. The cells, anodes, and cathodes are of the same type as used for zinc electrolysis. A typical plant is shown in Fig. 94. Sections of a cadmium electrolytic tank cell are shown in Fig. 95.

Each cell has 27 anodes and 26 cathodes, with spacings of 3.5 in. between cathode centers. Approximately 2.6 volts are used per cell, with a current density of 4.25 amp per sq ft (0.46 amp per dm²). The solution is fed to each cell individu-

ally, while the spent electrolyte discharges into a common collecting launder. The solution entering the cells contains 100 to 140 g per liter of cadmium and 65 g per liter of zinc; on discharge the electrolyte contains 70 to 80 g per liter of H_2SO_4. The for-
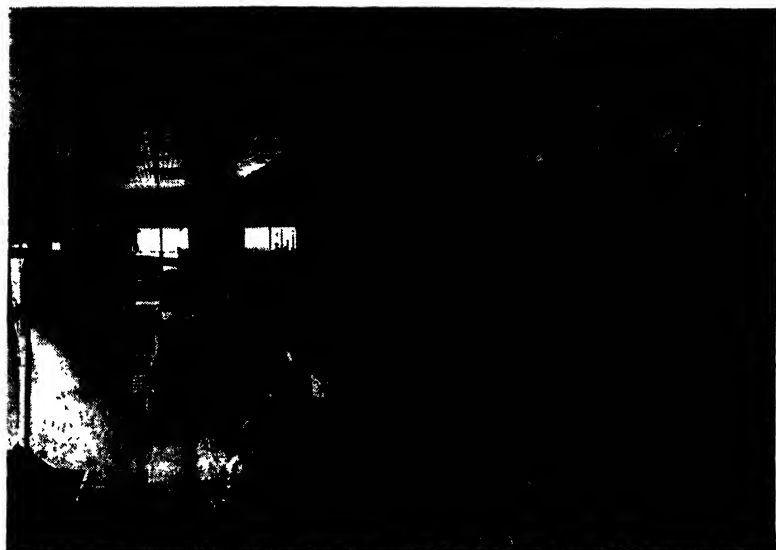
Fig. 94.   Electrolytic cadmium plant at Great Falls, Mont.   (*Anaconda Copper Mining Company.*)
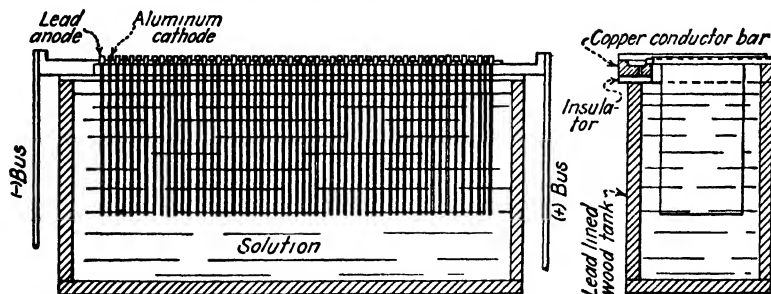
Fig. 95.   Section of cadmium cell.

mation of beads is lessened by maintaining the cell temperature at about 35°C as well as by adding an average of 10 lb of glue per ton of cathodes.

At 24-hr intervals the cathodes are removed, one plate at a time, and carried to the stripping rack.   The beads are scraped

TABLE 54. ELECTROWINNING OF CADMIUM

	Anaconda Copper Mining Company, Great Falls, Mont.	Consolidated Mining and Smelting Co., Trail, B.C.	Electrolytic Zinc Co., of Australasia, Ltd., Risdon, Tasmania	Hudson Bay Mining and Smelting Co., Ltd., Flin Flon, Manitoba	Sullivan Mining Company, Kellogg, Idaho	American Smelting and Refining Co., El Paso, Tex.
Raw material	Precipitate from Zn dust purification of Zn electrolyte	Zn dust purification residues from sulfide and oxide plants	Zn dust precipitate from Zn plant purification, Zn 35%, Cu 11%, Cd 8%	Zn dust purification residues	Zn dust purification residues	Precipitate from Zn dust purification of electrolyte
Electrolyte:						
Cd to cells, g/l	180	170	150	110		200
Zn to cells, g/l	50	72	30–40	66		30
Concentration H_2SO_4, g/l cell discharge	70–80	65	90	50		120
Temperature, °C	35	30	15–20	21		
Feed to cells	Cascade and individual	Cascade and individual	Individual	Cascade and individual		
Current:						
Current per cell	1,500	600	700–800	1947 Actual—300, capacity—750		2,000
Amp/sq ft	4	4 00	10–11	3	10	10
Voltage per tank	2 6–2 7	2 5	3 1	2 7		2.5
Current efficiency, %	80–90	90	88–92	85		
Kwhr/lb Cd	0 82	0.65 (d c.)	0 97	0.70 (d.c.)		

Anodes:						
Composition	Lead	Lead	Lead	Lead	Lead alloy	Lead
Size	45" × 24½" × 3/16"	9.2 sq ft submerged × ¼"	Roughly semicircular, approx. 21" radius, 5/16" thick	38" × 23" × 3/16"		31" × 19⅝" × 5/16"
Number	36	17	10	14		25
Mode of suspension	Cast around Cu header	Welded to busbar	2 mild steel bars 1½" × ¾" section with copper strip between them at contact end	Cast around Cu conductor	Cast around conductor	Weld to bar cast around conductor
Anode-cathode spacing, in.	3	2	2¾	3½		3
Cathodes:						
Number	36	16	9	13		24
Type	Al stationary	Stationary	Rotating	Stationary Al sheets	Stationary	Stationary
Size	45" × 24" × 3/16"	9.4 sq ft submerged × 3/32"	4' diam × ¼"	30" × 24" × 1/8" immersed		36" × 21" × 3/16"
Composition	Aluminum	Aluminum	Aluminum	Aluminum	Aluminum plates	Aluminum
Mode of suspension	Riveted to Cu header	Riveted to conductor	On 3" diam mild-steel shaft separated by rubber-covered Al sleeves	Welded to Al conductor with Cu insert at busbar contact		Welded to conductor
Removed after ? hr	48	24	48–96	24	12	12
Weight, lb	110	2 sheets, 2.0 lb each (Cd)	44	sheets, each 1½ lb		
Tanks:						
Length, width, and depth	10'3" × 2'10" × 4'9"	6'0" × 7'6" × 4'0"	5'0" × 5'0" × 2'6" sides sloping in at bottom	× 2'10" × 3'8"		7' × 2'6" × 4'6"
Number of anodes, cathodes	37, 36	17, 16	10, 9	14, 13		25, 24
Material of construction	Wood, lead-lined	Prodorite tanks	Wood, lead-lined, covered with 2" of sulfur sand mixture	Prodor te	Wood, lead-lined	Concrete, lead-lined

off and treated separately.   The cadmium sheets are washed with water, rolled into bundles, and dried in a steam oven.   The ampere efficiency for good sheets is 80 to 90 per cent.   The beads, which account for about 5 per cent of the metal, may be pressed together in a press, then sent to the melting furnaces with the sheet form of deposited cadmium.

The used electrolyte is returned to the tanks for leaching sponge.   To keep down the zinc content, a certain portion of this electrolyte must be replaced by concentrated H_2SO_4, if pure contact acid be available, or by spent zinc electrolyte of low zinc content.   The cadmium in the acid that is withdrawn may be recovered by precipitation on metallic zinc; or, to avoid the high zinc consumption, the acid may be used to leach zinc dust purification precipitate.

The dry cathodes are melted in cast-iron electrically heated pots of 1,000-lb capacity.   The temperature is maintained at about 400 to 450°C, a thin layer of caustic soda over the charge preventing excessive oxidation.   A steel hood over the pot keeps the oxide fume from entering the room.   The caustic becomes thick from oxidized cadmium and must be replaced at intervals.   About 40 lb of caustic per ton of metal is required.

Cadmium oxide and metallic beads and shots are contained in the caustic slag.   This is leached with water to dissolve the excess caustic soda, the solution decanted, and the oxide and beads treated with warm dilute H_2SO_4.   The metal is of such high purity, however, that it dissolves very slowly, the rate being markedly increased by the addition of MnO_2.   The leach solution is filtered and fed to the electrolytic cells.

The cadmium tapped from the pots is cast in 75-lb bars, which are remelted and cast into salable forms, such as pencils, slabs, anodes, and balls.   The purification flow sheet for cadmium recovery from the residues resulting from the treatment of both the sulfide and oxide ores at Trail is given in Fig. 96, while the operating data for the plant are given in Table 54.

At the Flin Flon plant of the Hudson Bay Mining and Smelting Co., Ltd., the residue from the zinc-dust purification in the leaching plant is leached in zinc cell acid to dissolve the zinc and cadmium.   The leach is filtered and the filtrate passed through hot vats, in which are suspended zinc castings.   Cadmium is precipitated by cementation as a sponge, and the barren solution

after purification is returned to the zinc plant. The sponge after oxidation is leached hot with fortified cadmium cell acid, filtered, and the solution purified of cobalt and thallium, using $KMnO_4$ and lime. This yields a solution suitable for electrolysis of

Sulphide sponge   Oxide sponge

Stock bins

Lime rock → Mechanical agitator (Steam-heated)

Kelly filter

Filtrate   Residue

Mechanical agitator (Steam-heated)

$KMnO_4$
CaO

Kelly filter

Filtrate   Residue

Electrolysis

Return acid   Cathodes

Washed and dried

Oxide return acid

Mechanical agitator

Kelly filter

Filtrate   Residue

Oxide plant

Precipitating tank

Filter box

Filtrate   Sponge

Oxide plant

25 Percent   75 Percent

Primary melting furnace

Caustic soda

Rough bars

Caustic soda

Slag

Finishing furnace

Dissolving box

Metal prills

Slag

Retreatment furnace

Cadmium metal
to market

Metal   Slag

Fig. 96.   Flow sheet of the cadmium recovery plant at Trail.   (*Engineering and Mining Journal.*)

composition Zn 65.1 g per liter, Cu 0.004 g per liter, Cd 91.4 g per liter, Co 0.127 g per liter. This solution is electrolyzed at 3 to 4 amp per sq ft, in equipment identical with that in the zinc tank room except bussed with aluminum. Twenty cells of 2.7 volts per cell in four cascades of five are used. Current efficiency averages 82.0 per cent, cell temperatures 21°C, and the deposited sheets, two per cathode about 1 lb each, are stripped

daily. Electrodes and deposition tanks showed no deterioration after 2 years.

The overflow from electrolysis, cadmium cell acid, has the composition: Zn 67.1 g per liter, Cu 0.003 g per liter, Cd 30.2 g per liter, Co 0.127 g per liter, H_2SO_4 56.2 g per liter. Stripping the cadmium to below 25 g per liter results in poor deposition and current efficiency. The deposited cadmium, stripped daily from the aluminum cathodes, is washed, dried, melted with puddling under caustic soda, and cast into commercial slabs, balls, and pencils. Operating data are given in Table 54.

Electrogalvanizing from Leach Liquors. Tainton[22] described the application of electrowinning methods to electrogalvanizing. Coils of iron wire are butt-welded together for continuous zinc plating. The wire to be galvanized is cleaned cathodically in fused caustic. Sodium metal is liberated, which removes all nonmetallics such as silicon, sulfur, and phosphorus. The iron oxide is reduced to the metallic iron state. The caustic pickle tank is a steel pan 20 ft long, 24 in. wide, and 12 in. deep. Raw material consists of roasted concentrates containing about 69 per cent Zn. The zinc is dissolved in spent electrolyte (25 per cent H_2SO_4) from the cells. The residual compounds of iron, silicon, and lead and related gangue are separated, and the resultant solutions are purified free from copper, cadmium, cobalt, and the like by treatment with zinc dust. The zinc solution is drawn into the plating cells at the same speed that the zinc is removed from the cells by the plating action; four cells each take 15,000 amp at 4 volts. The steel, lead-lined cells are 55 ft long with 8 wires in each cell. Because of the approximately 2,000 amp per wire, contacts (lead with 1 per cent silver) are provided every 3 ft to prevent the total current from flowing through any one point of the wire and melting it. Deposition of 1 oz per sq ft in about 45 sec is realized.

The zinc deposited is of a mat or crystalline type which is smoothed and compressed by rotary polishers before coiling. Coatings are made up to 4 oz per sq ft for wire that is to be drawn down into finer sizes such as screen wire. At some plants the wire is annealed in a gas-fired furnace to burn off the grease, passed through the acid and anodic pickling and into the 110-ft plating cells drawing 40,000 amp each, 12 wires being plated

[22] TAINTON, U. C., *J. Am. Zinc Inst.*, **18**, 42 (1937).

simultaneously, and then passed through dies to brighten and to densify the surface. The electrolyte to the cells contains 200 g of zinc per liter and 200 to 270 g of H_2SO_4 per liter. The current density on the cathodes is of the order of 700 to 2,000 amp per sq ft, at which current density a large gas evolution occurs. The anodes are lead-silver alloys. The wire travels at a rate of 50 to 200 fpm.[23]
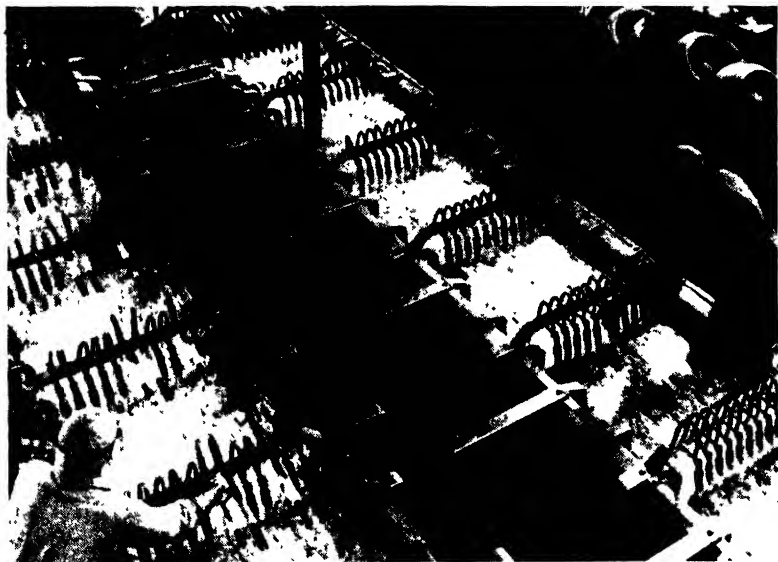
FIG. 97. Cells for the electrogalvanizing of wire. (*Bethlehem Steel Co.*)

The process allows the use of low-grade concentrate carrying 30 per cent zinc. Electrogalvanizing as compared to hot dipping shows less of the bonding zinc alloy, a brittle constituent causing failure of the coating owing to breakage or cracking of the bond. Silicic and cresylic acids are used on top of the plating tanks as a prevention against the acid spray. A typical cell is illustrated in Fig. 97.

ANTIMONY

Electrolytic antimony is produced by electrowinning from argentiferous tetrahedrite, a silver-copper-antimony sulfide which cannot be broken down physically and separated. It is concen-

[23] SHELTON, S. M., and ROYER, M. B., *Iron Age*, Apr. 23, 1936, p. 44.

trated away from pyrite. The tetrahedrite is batch leached with hot sodium sulfide solution, settled, and filtered. The leach liquors are batch electrolyzed in diaphragm cells. In a non-diaphragm cell the S^{--} of the sodium sulfide which is used as the solvent is oxidized to S^-, forming Na_2S_2 at the anode. This becomes sufficiently concentrated as the electrolysis proceeds to inhibit and finally prevent the deposition of antimony at the cathode. The end result of the electrolysis of a batch of solution in an open cell is to redissolve the antimony which had precipitated on the cathode at the beginning of the electrolysis. It was found that during the leaching and electrolysis steps, using this concentrated sodium sulfide solution, various oxidation products build up in the solution, characterized by the following types: sodium sulfite, Na_2SO_3; sodium thiosulfate, $Na_2S_2O_3$; and sodium sulfate, Na_2SO_4; as well as some sodium carbonate, Na_2CO_3. These are of no aid as regards the solution of antimony, and the efficiency of the solvent in decomposing the tetrahedrite rapidly falls off.

Both catholyte and anolyte liquors from the cells are regenerated with barium sulfide solution and recycled. The barium precipitates are reduced to barium sulfide by coal and reused in further cycles. During the electrolysis, part of the sulfur of the catholyte migrates to and concentrates in the anolyte, while part of the sodium of the anolyte migrates to and concentrates in the catholyte. The cell reactions are: The antimony deposits on the cathodes. Sulfur concentrates in the anolyte, forming among other compounds sodium polysulfide, Na_2S_2; sodium sulfite, Na_2SO_3; sodium thiosulfate, $Na_2S_2O_3$, and sodium sulfate, Na_2SO_4. The alkalinity of the anolyte decreases, but that of the catholyte increases.

The operating data are given in Table 55.

At the Bunker Hill and Sullivan Mining and Concentrating Co., Kellogg, Idaho,[24] tetrahedrite ($3Cu_2S \cdot Sb_2S_3$) concentrates mixed with sodium carbonate, sodium sulfate, and coal are fed to a three-electrode electric furnace. Current at 50 to 110 volts, flowing from electrode to furnace wall, the charge serving as the resistance, yields a melt temperature of about 2300°F. Matte is tapped from the furnace, cooled, and crushed to pass 80 mesh. The ground matte is leached with water at 140°F to form the electrolyte. Undissolved pulp is crushed and tabled to yield a

TABLE 55. ELECTROWINNING OF ANTIMONY

Size of batch, tons . . .	5
Leaching tanks...	4–22 tons of solution each
Leach solution:	
Na_2S, g/l........ .	250
Sb, g/l	10
Leaching time, hr	8–10
Leaching temperature, °C	100–103
Electrolyte:	
Na_2S, g/l	100
Cells:	
Number	. 96
Arrangement	Cascades of 6
Length $\times$ width $\times$ depth	60″ $\times$ 32″ $\times$ 30″
Anodes:	
Number	8
Material	Mild steel, ⅛ in. thick
Spacing, in	2½
Area	3 sq ft per side
Cathodes:	
Number ...	9
Material ..	Mild steel, $\frac{3}{16}$ in. thick
Area..	3.33 sq ft per side, 53.3 sq ft per cell
Removed after ? days	3
Diaphragm .	Canvas
Life, days	15–20
Anolyte feed	Across face of anode
Manner .	Gravity from head tanks
Composition, feed, g/l NaOH	225
Composition, exit, g/l NaOH	175
Catholyte feed .	Near bottom of cell
Manner.	By gravity from head tanks
Composition, feed	250 g/l NaOH, 50 g/l Sb
Composition, exit	280 g/l NaOH, 8–10 g/l Sb
Current, total, amp	1,500
C. d., amp/sq ft...	28
Voltage per tank...	2 5–3 (2.65 av.)
Generators.	Two 750 amp, 300 volts, connected parallel
Analysis of product:	
Per cent Sb	96–97
Per cent As . . .	2–3
Per cent Cu, Pb, Fe, Bi.	Less than 0.4

concentrate of Sb-Bi-Ag alloy and a tailing containing 25 to 30 per cent Cu and 1 per cent Sb, the latter being added to the copper smelter charge. From the electrolyte containing the thioantimonate (Na_3SbS_4), antimony is deposited upon sheet-steel cathodes. The anodes are sheet lead.

There is no material corrosion of either electrode at operating current density of 20 amp per sq ft. Cathodes are stripped of their antimony every 6 days. Spent electrolyte containing about 2 to 5 g per liter is recycled to the leaching tanks. The antimony, being brittle, is easily removed from the cathodes.

COBALT

Experimental electrowinning of cobalt from complex cobaltite ores has been reported[25] involving (1) roasting the concentrates, (2) leaching the calcine with caustic, (3) leaching the caustic-leach residue with sulfuric acid, (4) precipitation of arsenic from acid leach solution, including precipitation of ferric Fe, (5) H_2S treatment to remove acid-sulfide group metals and zinc, (6) Fe purification, (7) precipitation of pure $CoCO_3$, and (8) electrolysis of $CoSO_4$ solution, using the pure $CoCO_3$ as neutralizing agent for spent electrolyte.

Two different types of electrolyte were used for cobalt electrowinning. The first was a fluoborate electrolyte containing about 50 g per liter boric acid, 5 g per liter sodium fluoride, and 20 g per liter Co as $CoSO_4$, although tests were made on one containing 27 g per liter cobalt. The second electrolyte, as proposed by Roentgen and Giesen,[26] contained only $CoSO_4$ and incidental salts. This electrolyte contained 40 g per liter Co.

Cell temperatures were 60°C, current density 25 amp per sq ft, with lead anodes and stainless-steel cathodes. The cobalt metal was 99.2 per cent Co and 0.74 Ni, with traces of Si, Mg, Pb, Al, Fe, Ca, and Cu. Current efficiencies ranged from 69 to 85 per cent with cobalt concentrations of 25 to 100 g per liter and d.c. power requirements from 1.56 to 1.2 over the same range.

CHROMIUM

Experimental production of electrolytic chromium by electrowinning methods from low-grade ores from Western states of the United States has been carried out by the Bureau of Mines.[27]

Finely ground chromium ore is leached with H_2SO_4 and cell anolyte. Filtered solution is crystallized to produce a chrome

[25] SHELTON, F. K., CHURCHWARD, RUTH E., STAHL, J. C., and DAVIS, C. W., *Trans. Electrochem. Soc.*, **91**, 115–131 (1947).

[26] ROENTGEN, PAUL, and GIESEN, KURT, *Metall u. Erz*, **39**, 28–32 (1942).

[27] LLOYD, R. R., ROSENBAUM, J. B., HOMME, V. E., and DAVIS, L. P., *J. Electrochem. Soc.*, **94**, 122–138 (1948).

alum which is purified and used for electrolyte preparation.   Cell liquor composition and permissible impurities are given in Table 56, and operating details in Table 57.

TABLE 56.   ANALYSES OF CELL FEED AND PERMISSIBLE CONCENTRATION OF IMPURITIES

Component	Concentration, g/l	Permissible concentration, g/l
Cr	90 5	
NH₃	29.5	
Na	16.9	
Fe	0.3	
Al	0 030	0 125
Mg	0 080¹	0 100
Pb	0 001	0 002
Ni	0 001	0 004
Ti	0 003	Not critical
Mo	< 0 0005	Not determined
Mn	Trace	Not critical
Co	Nil	Not determined
Ca	Nil	Not determined
SiO₂	Nil	Not determined

¹ Mg enters the cell feed with recovered sodium sulfate.

TABLE 57.   TYPICAL CELL OPERATING DATA FOR ELECTROLYTIC CHROMIUM

Cathode area	10 sq ft (92.9 dm²)
Cathode material	Aluminum bronze
Rate of catholyte flow	0.3 gal/sq ft/min (0.12 liter/dm²/min)
C.d.	67 amp/sq ft (7.3 amp/dm²)
Cell potential	4.3 volts
Current efficiency, %	60.6
Kwhr/lb metal	5.0 (11.0 kwhr/kg)
pH	2.25
Na₂SO₃ addition, g/l/hr	0.0034
Goulac addition, g/l/hr	0.0015
Temperature, °C	46
Analysis of product, %	98.8 Cr, 0.4 Fe, 0.01 S, 0.03 H₂, 0.17 O₂

Electrolyte analyses	Catholyte	Anolyte
Cr	35.0	23.7
NH₃	47.5	11.2
Na	25.0	7.9

IRON

The production of electrolytic iron by leaching methods employing pyrrhotite ores was begun by Eustis in 1920, and an experimental plant was built at Milford, Conn.[28] The deposition cell contained a cylindrical steel mandrel cathode separated from graphite anode plates by an asbestos-cloth diaphragm. Cells were operated at 80 to 90°C at current density of 100 amp per sq ft (10.8 amp per dm^2) at cell voltages of 4 to 4.4. Best operating conditions were an iron content of 170 to 185 g per liter, an absence of ferric iron in the catholyte, and pure electrolyte at a pH of 3.7 to 3.9, when cathodic current efficiencies of 94 per cent were obtained.

The production of electrolytic iron from sulfide ores has been studied.[29] Pilot-plant operation has shown the possibility of producing pure iron in dense homogeneous form by leaching sulfide ores with ferric chloride. The process requires the use of a diaphragm cell and a hot electrolyte. When sulfide ores contain other metals, these are recovered as by-products. None of the leaching processes ever reached the commercial stage.

MANGANESE

Electrolytic manganese is the product of an electrowinning operation. Manganese ores, if not already acid soluble, are conditioned by reduction procedures. Their manganese values are extracted by a sulfuric acid leaching solution, which is an anolyte from the electrolytic cells. The leach solution after increase in manganese content and decrease in acid is carefully purified, and after adjustment becomes the feed liquor to the deposition cell where insoluble anodes are employed. The feed liquor enters the catholyte chamber of a two-compartment diaphragm cell where the manganese content of the feed is stripped, the solution passing through the diaphragm to become part of the anolyte. Anolyte returns in circuit to leach fresh conditioned ore, and the cycle is thus continuous.

Following the early work of the U.S. Bureau of Mines carried on in pilot plants using domestic ores, a translation to a com-

[28] BELCHER, D., *Trans. Am. Electrochem. Soc.*, **45**, 455 (1924).

[29] PIKE, R. D., WEST, G. H., STECK, L. V., CUMMINGS, R., and LITTLE, B. P., *Trans. Am. Inst. Mining Met. Engrs.*, **81**, 311 (1930).

mercial plant was attempted. Unfortunately many difficulties appeared on a larger scale, which troubles had not been encountered in the pilot plant. The first plant was far from an operating success. Even if the plant had operated, expected production costs were shown to be far too optimistic.

The commercial manufacture of electrolytic manganese was developed by the Electro Manganese Corporation. Wana-
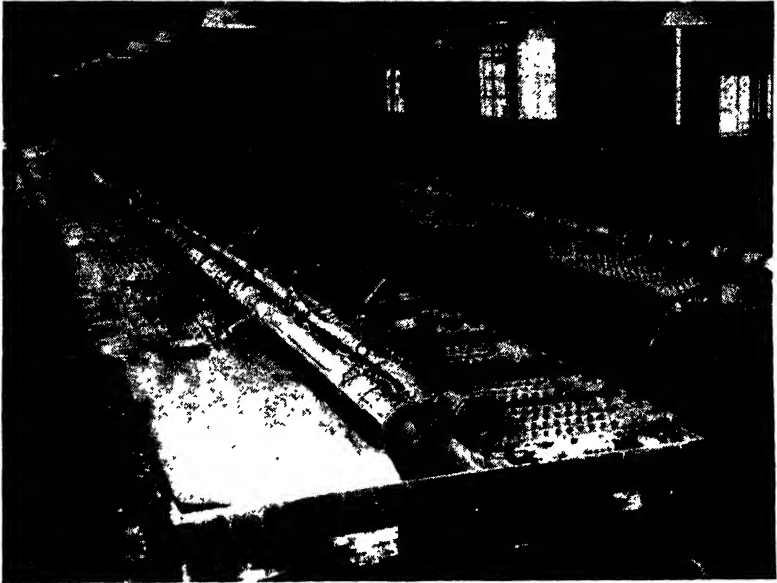
Fig. 98. Cell room for the production of electrolytic manganese. (*Electro Manganese Corporation.*)

maker[30] described the operations at Knoxville, Tenn. A portion of the cell room is shown in Fig. 98.

Manganese metal of high purity may be made by electrowinning in contrast to the special ore requirements for electric furnace processes producing less pure manganese metal. A wide variety of ores ranging from Chamberlain, S.D., and Arkansas carbonates, to imported high-grade oxides mixed with local oxide tailings plus by-product solution from a nearby chemical plant have been used. Oxide ores of the pyrolusite type are not soluble in anolyte but must be reduced. The use of carbonate

[30] WANAMAKER, E. M., *Trans. Am. Inst. Mining Met. Engrs.*, **159**, 428 (1944).

ores proved, in spite of their direct solubility, to be more expensive than reduced oxide ores, because of higher freight costs per unit of manganese coupled with very high acid consumption and large amounts of residue.   Most ores can be successfully treated, but obviously the lower grade ore mixtures require more equipment for such steps as grinding, reduction, settling, and filtering.
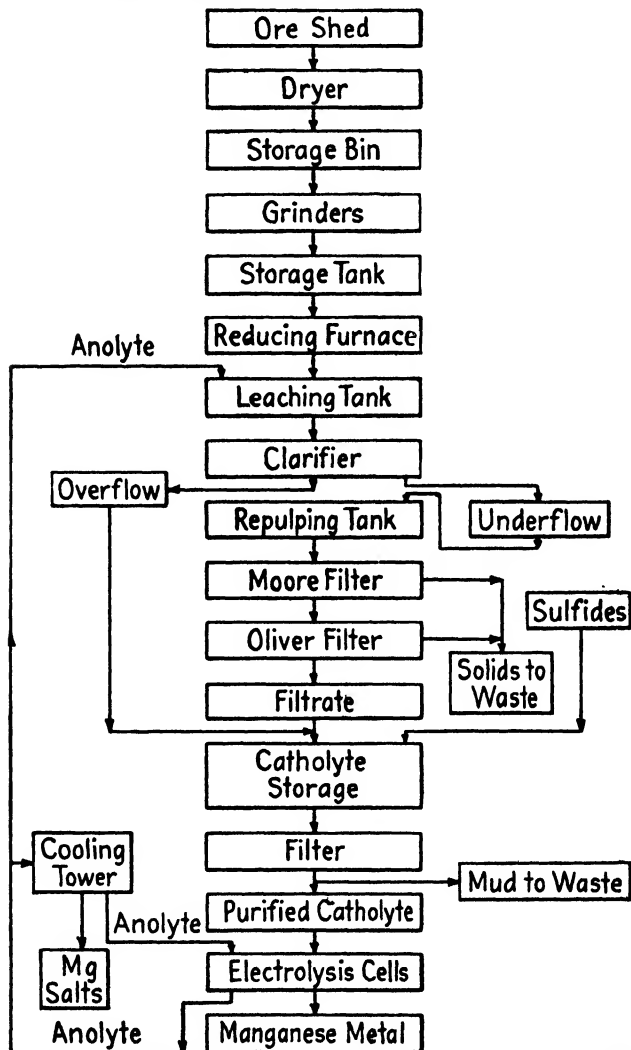
FIG. 99.   Flow sheet for the production of electrolytic manganese.

TABLE 58. DATA ON PRODUCTION OF ELECTROLYTIC MANGANESE

Average manganese content of ore, % . .	48
Coarse grinding . . .	Jaw crusher and gyratory
Fine grinding	Raymond mill
Reduction furnace. . .	Two 12-in I.D. alloy-steel tubes, 15 ft long with 15-ft cooler
Heating method .	Resistance by nickel-chrome alloy units
Furnace capacity, ore per day per furnace	15 tons
Reduction, %	99
Thickeners, Dorr .	Two 40 ft diam, 90,000 gal each
Leaching tanks . .	Six 8,000 gal each
Purification tanks.	Eight 10,000 gal each
Anolyte:	
Mn, g/l, as $MnSO_4$ . . .	10–18
H_2SO_4, g/l.	25–35
$(NH_4)_2SO_4$, g/l. . .	120–150
pH value	1–.4
Catholyte feed:	
Mn, g/l, a $MnSO_4$	25–35
$(NH_4)_2SO_4$, g/l	125–135
pH value.	7 2–7 6
Anodes:	
Material.	Lead alloy
Number per cell . . .	21
Cathodes:	
Material.	Stainless steel
Size	$36'' \times 18'' \times \frac{1}{16}''$
Number per cell .	20
Cell amperage	6,000
Cell temperature, °C	35–40
Cathode c.d., amp per cell	40
Diaphragm material	Textile
Diaphragm life . .	8 weeks
Cell voltage.	5
Current efficiency, %	65–70
Recovery to metal, %	87
Operating time for cathodes, hr	24–40
Kwhr/lb metal (d.c.)	4–4.5
Kwhr/lb metal (a.c. over all)	5–5.25
Purity of manganese, %	99.97

The flow sheet of the process is given in Fig. 99 and the operating data for the plant in Table 58.[31]

In the preparation of electrolyte from which the metal is deposited, the solution is purified completely of impurities such

[31] MANTELL, C. L., *Trans. Electrochem. Soc.*, **94**, 232–243 (1948).

as iron, arsenic, antimony, tin, lead, nickel, cobalt, molybdenum, silica, aluminum, while calcium and magnesium are removed by special methods.   At Knoxville, diaphragms are around the cathodes, and the anolyte fills the cell around the diaphragms.

The electrowinning of manganese depends on very pure solutions.   In addition, there is dependence on a combination of factors such as concentration, pH, temperature, current density, cathode and anode material, rate of flow to the cells, as well as other variables.   Problems of dealing with an alkaline catholyte and an acid anolyte in a two-compartment cell, as well as the impossibility of considering any of the variables separately because of their influence on each other, cause manganese electrowinning to be almost in a class by itself.   It demands much more delicate control than does the electrowinning of zinc and copper, for it carries all their problems and many more.

CHAPTER 17

ELECTROLYSIS OF ALKALI HALIDES AND SULFATES

Before the Second World War, electrolysis of sodium chloride for the preparation of chlorine and caustic was, with the exception of small amounts of potassium hydroxide, the major electrochemical process. Chlorate and perchlorate production was confined largely to Europe. During and after the war, fluorine chemistry developed rapidly, the United States became a major producer of chlorates (discussed under oxidation and reduction products, Chap. 7) and the electrolysis of sodium sulfate became of importance. Mercury-type cells found increasing application, particularly in large amperage units.

CHLORINE AND CAUSTIC

Cruikshank observed the evolution of chlorine upon passing an electric current through a solution of sodium chloride as early as 1800. A period of some fifty years elapsed before marked progress in the development of electrolytic chlorine is shown in the patent literature. The patents recorded for various types of electrolytic cells are numerous from the year 1885, and a few installations appearing about 1890 embodied features that made for their commercial success. In America the first commercially successful electrolytic chlorine plant was built at a paper mill in 1890.

Chlorine was first produced on an industrial scale from salt, H_2SO_4, and MnO_2, and later by the oxidation of HCl to chlorine. These procedures have been entirely replaced by electrochemical processes involving the electrolysis of alkali halides, generally NaCl or KCl, with the production of chlorine at the anode and NaOH or KOH plus hydrogen at the cathode. Inasmuch as chlorine and alkali hydroxides react to form hypochlorites according to the reaction

$$Cl_2 + 2NaOH \rightarrow NaOCl + NaCl + H_2O$$

these as well as chlorates may be formed if the anodic and cathodic products be allowed to mix. In commercial cell design and operation, precautions are taken to prevent mixing of the products of the electrolysis and to remove them from the cells as rapidly as possible.

Economically, in the United States the primary product of salt electrolysis is chlorine, while caustic is the secondary or by-product. Outside of the United States the reverse is often true. Companies engaged in the electrolysis of salt were considered as members of the chlorine industry, primarily concerned in making chlorine and finding uses for it. Electrolytic caustic formerly amounted to about one-third of the total caustic made and consumed in the United States, but by 1940 was one-half, with continued growth so that electrolytic caustic shortly became the major source. By-product hydrogen from salt electrolysis finds use in the manufacture of synthetic ammonia and in smaller amounts in the production of HCl produced by combustion of hydrogen in chlorine. In a special case the hydrogen is used by one producer for hydrogenation of oils.

In 1926 about two-thirds of all the chlorine gas manufactured in the United States and Canada was consumed by the paper industry; 22 per cent was used in the textile industries; 10 per cent in sanitation, and the remaining 3 per cent in all other uses.[1] By 1936 as the result of chlorine utilization for the manufacture of ethylene glycol, carbon tetrachloride, chlorinated naphthalene, and bromine as well as chlorinated hydrocarbons, production was twice that of 1926. Approximately one-third of the chlorine was used for bleaching pulp, 5 per cent for textiles, one-half for chemical manufacture, 6 per cent for sanitation, and the remainder for all other uses.

By 1946 approximately 20 per cent of the total caustic was consumed in the manufacture of rayon, a little more than 5 per cent in the production of soap, about the same for the bleaching of pulp and paper, approximately 6 per cent for textiles, approximately 20 per cent for direct chemical manufacture, and an additional 20 per cent for indirect preparation of other chemicals, about 5 per cent for sanitation, 6 per cent for petroleum refining, about 5 per cent for lyes and cleaners, less than 2 per cent for rubber reclaiming and vegetable-oil refining, and the balance for

[1] PRITCHARD, D. A., *Trans. Am. Electrochem. Soc.*, **49**, 39 (1926).

a number of miscellaneous uses. By 1946 the caustic production was considerably more than double the 1936 output.

While the electrolytic cell is the heart of the electrolytic chlorine and caustic soda plant, from the chemical engineering viewpoint many other pieces of equipment are necessary for the production of the final material. This will be illustrated by the flow sheet, Fig. 100. Brine is heated, purified by precipitation of the heavy metals as carbonates, and the temperature-controlled solution is fed to the electrolytic cell. In the case of the more common diaphragm cells, a weak caustic solution containing an appreciable quantity of salt, as well as chlorine and hydrogen gas, results. The weak caustic solution goes to evaporators where it is concentrated and the salt crystallized and filtered out. The strong caustic solution then goes to direct-fired finishing pots to be converted into solid or flake caustic. In the case of the mercury cells, caustic solutions of much higher concentration may be produced. These are either sold as liquid caustic or sent to finishing pots for the preparation of solid material. The product of the mercury cells is free of salt. Chlorine from either type of cell is cooled, dried, refrigerated, and liquefied. Hydrogen is either sent to waste or collected and employed for the manufacture of HCl gas by combustion with chlorine, or the manufacture of ammonia by combination with nitrogen, or in some cases sold as hydrogen in compressed form.

Anodic and Cathodic Processes. The anodic and cathodic processes in alkali-chlorine cells are affected by the materials used for electrodes, the temperature, concentration of electrolyte, its purity, current density, cell construction, and other factors. At the anode, chlorine is discharged and, if conditions be favorable, may react with water to give ClO^- ions or free $HClO$, which by self-oxidation may give rise to chlorites, chlorates, and oxygen with the development of acidity in the electrolyte.

In the mercury cell, sodium ions are discharged at the cathode, where they alloy with the cathode. In the diaphragm type of cell with a sheet-metal cathode, hydrogen, as a result of the low hydrogen overvoltage of the cathode material, is discharged preferentially to sodium, and hydrogen gas is evolved. The sodium ion and the hydroxyl (remaining from the ionization of the H_2O which furnished the H^+) unite to become the cathode film product $NaOH$.
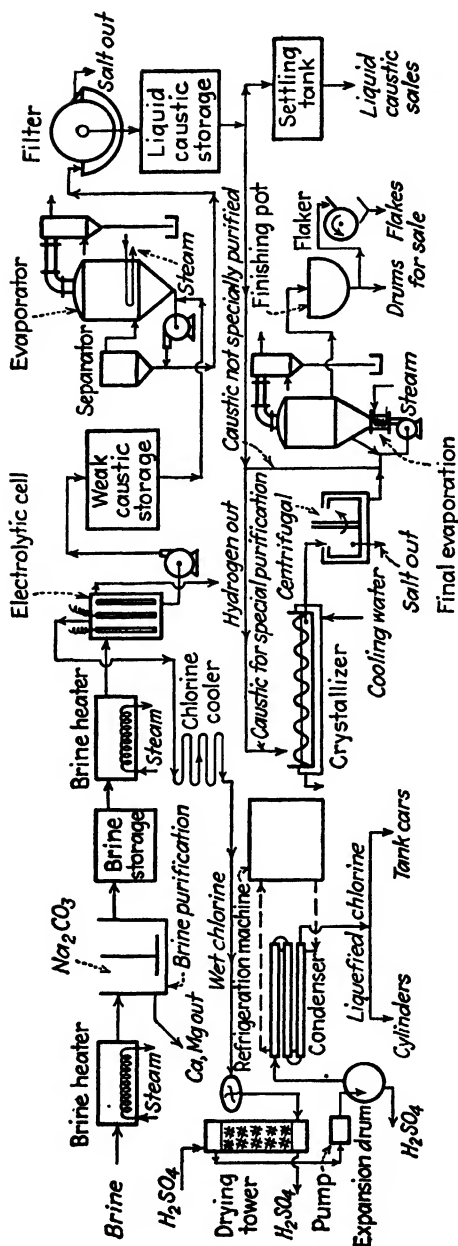
Fig. 100. Electrolytic caustic soda and chlorine. (*Chemical Engineering.*)

If a NaCl solution be electrolyzed under such conditions that the current density at the electrodes be kept constant (the voltage regulated to maintain this condition), the electrode products be kept separate, and no salt additions be made to the cell, there will be hypochlorite formation. The Cl^- ion concentration will decrease and the HClO concentration will increase if the chlorine in solution remain constant or increase. The HClO is only little ionized, its dissociation constant being 3.7×10^{-8} at 20°C. If the current be maintained, higher cell voltages and higher anodic polarization will be needed, ClO^- ions will discharge, oxygen will be evolved, and chlorates will form. As the Cl^- ion concentration decreases with continued electrolysis, greater portions of the current will be used up in chlorate production. The high ionic mobility of the H^+ ion will cause its rapid migration from the anode area, so that acidity, increase of which would aid HClO formation, remains low. Increasing oxygen evolution will dilute the chlorine and reduce its solubility (owing to lower partial pressure of the chlorine in the atmosphere above the electrolyte), and the rate of formation of HClO will decrease. Therefore, during electrolysis of a static NaCl solution, HClO formation and the portion of current producing chlorate are low at the beginning, gradually increasing and reaching a peak value; but with decreasing concentration of NaCl in the electrolyte, they will decrease. At constant current the anode potential reaches a critical point where OH^- ion discharge with oxygen evolution takes place, and the partial pressure of chlorine is reduced, with decreased solubility of the gas in the electrolyte. It will therefore be seen that, during the course of electrolysis of salt at constant current under conditions in which the products of electrolysis are not allowed to mix and no further salt is added to maintain concentration, the chlorine evolution diminishes continually throughout; the HClO concentration of the electrolyte and the chlorate formation increase to a maximum and then fall off; while the oxygen evolution due to OH^- ion discharge increases continuously throughout the course of the electrolysis.

In commercial electrolysis of salt, the formation of hypochlorite and chlorate is avoided by maintaining the electrolyte in a saturated condition. Thus the Cl^- ion concentration is maintained at a more or less constant rate. At the same time an advantage is obtained in that the solubility of chlorine gas in

saturated salt solutions is less than in those of a more dilute nature.

Anodes. The anode material should preferably be chemically inert, be as mechanically strong as possible, be inexpensive, show good electrical conductivity, and have low chlorine overvoltage, as the anode potential is determined by the discharge of Cl^- ions and the evolution of chlorine gas. The chlorine overvoltage is high at smooth platinum anodes. Platinum anodes are now obsolete. Their high cost requires the use of high current density, with resultant high voltages. With magnetite anodes which are cheap, low current densities are advantageously used. Magnetite anodes have the definite disadvantage of being very fragile, and usable only in the cast form. They do not have the machinability of metals or graphite. In the United States they find no application. Graphite anodes show lower chlorine overvoltage than do platinum. At the surface of graphite anodes the formation of chlorate will start later than at platinum or magnetite under the same conditions. On the other hand, graphite requires a lower overvoltage for OH^- ion discharge, so that oxygen evolution will commence earlier and will take a larger fraction of the total current than in the case of magnetite or platinum. In the case of graphite, medium current densities are employed so that the greater part of the electrolysis will take place on the surface. Dense, homogeneous, and compact anodes aid in the production of purer chlorine gas.

Graphite anodes are universally used. Graphite anodes are commonly impregnated with oxidizable oils of the drying type or with resinous substances or other materials to increase their apparent density and to reduce porosity. With porous graphite anodes the electrolyte in the anode becomes depleted far more quickly than the main bulk of the solution, with the resultant setting in of oxygen evolution, oxidation of the anode, and the production of CO_2 impurities in the chlorine.

Disintegration of anodes with necessary replacement is a factor in commercial cells, but anodes last from 1 to 3 years. Graphite consumption is of the order of 5 lb or less per ton of chlorine produced.

Cathodes. The cathode materials should be cheap, be readily fabricated, be mechanically strong if used in solid form, and, inasmuch as Na^+ ion cannot be readily discharged at metallic

electrodes, should have a low hydrogen overvoltage. The single electrode potential for a normal Na^+ ion solution at which Na^+ ion is discharged is -2.714, whereas H^+ ion requires only -0.4 volt. It will be seen that hydrogen evolution will occur much more readily on metals such as iron, copper, and nickel. In the case of mercury with a high hydrogen overvoltage, which value rises sharply with increases in current density, the Na^+ ion is preferentially discharged and forms an alloy with the cathode metal. At high current density as the result of the effect of increased current density on hydrogen overvoltage at cathodes of lead, platinum, and tin, Na^+ ion discharge takes place with alloying of the cathode, followed by chemical reaction of these alloys with the water of the electrolyte and the evolution of hydrogen gas. The surfaces of the cathode materials are physically broken up, and in commercial operation these disintegration products must be treated to restore them to normal condition.

Inasmuch as iron shows a lower hydrogen overvoltage than copper, nickel, graphite, tin, or aluminum, is cheaper, and is not attacked to too great an extent by alkalies or alkaline solutions of NaCl, it is the universally accepted cathode material for diaphragm cells as well as for those varieties of mercury cells where the mercury is an intermediate electrode.

In the earliest forms of the mercury cell, the mercury acted as a bipolar electrode, in that it is cathode in the section in which salt electrolysis takes place and anode in the denuder section where sodium hydroxide is formed. If, in operation, the mercury cathode become saturated with $NaHg_2$ and contain some Na_3Hg, so that from 0.5 to 0.8 per cent Na is present, Na^+ ion is discharged at about -2.0 volts; but if, as a result of mercury circulation, the sodium metal content be kept as low as 0.2 per cent, the Na^+ ion will discharge at about -1.83 volts.

Hydrogen ion discharges at a potential of about -0.4 volt plus an overvoltage (at low current density at mercury) of between 0.9 to 1.12, which is in turn increased in value at a sodium alloy surface in contrast to mercury. The hydrogen potential will be further increased, say to -0.6, in that the electrode surface film will be alkaline, owing to sodium metal reaction, and not neutral. Operation current density and temperature will increase the hydrogen overvoltage so that the total

potential for hydrogen evolution will be of the order of -2.0 volts, or greater than that for Na^+ ion discharge.

Formation of sodium amalgam is possible only because of the high overvoltage of hydrogen on mercury. The potential between a saturated sodium chloride solution and 0.2 per cent sodium amalgam is -1.83 volts. The overvoltage of hydrogen on mercury at the usual current densities is about 1.30 volts. The pH of the solution next to the amalgam is probably about 9 so that the equilibrium hydrogen discharge potential would be about -0.61 volt and the potential for hydrogen discharge would be -1.91 volts. At the cathode, the reaction with the most positive potential takes place so that sodium instead of hydrogen is discharged.

However, hydrogen discharge always takes place to a slight extent. It is increased if (1) the sodium ion concentration gets too low, (2) the temperature becomes too high, (3) the sodium concentration of the amalgam increases too much, or (4) impurities are present to electrolyze out on the mercury surface and there decrease the hydrogen overvoltage.

Common impurities in salt, such as calcium, magnesium, and iron, alone do not cause amalgam discharge, but nickel and cobalt do. Iron in brine containing either calcium or magnesium promotes amalgam discharge. Hydrogen discharge depends not only on the concentration, purity, and temperature of the brine, but on the sodium concentration of the amalgam. This, in turn, depends on the denuding cell.

Gardiner[2] outlined the action of the denuding cell as follows:

In the denuding cell, sodium amalgam acts as an anode and is short-circuited to a cathode, the electrolyte being sodium hydroxide solution Reactions are as follows:

$$\text{Anode: } NaHg_x - e = Na^+ + xHg$$
$$\text{Cathode: } H_2O + e = OH^- + \tfrac{1}{2}H_2$$
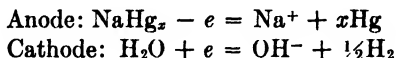
Sufficient water must be fed into the cell to supply the cathode reaction and to carry away in solution the sodium hydroxide formed. The escape of hydrogen also evaporates water from the solution. Solutions containing 30 to 50 per cent sodium hydroxide are made directly in the cell.

Sodium amalgam reacts with water very slowly because of the high

[2] GARDINER, W. C., *Chem. & Met. Eng.*, **52**, 110 (July, 1945).

voltage of hydrogen on the amalgam surface. It can be speeded up by placing a metal having a low hydrogen overvoltage in contact with the amalgam and the solution. This is a voltaic battery; component potentials are illustrated in Fig. 101. The driving force of the cell is the sodium amalgam anode potential e_1. Opposing it are the anode polarization e_2, the potential to overcome the resistance of the sodium
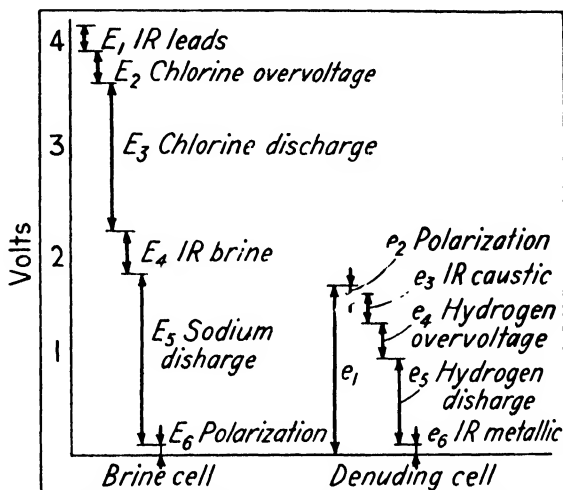
FIG. 101. Voltage components of a mercury cell.

hydroxide solution e_3, the hydrogen overvoltage of the cathode e_4, the equilibrium hydrogen discharge potential e_5, and the potential required to overcome metallic resistance e_6.

Amalgam anode discharge potential is the voltage between the anode and the solution. It may be calculated from the activity of the sodium in the amalgam and the activity of the sodium ion in the solution. It is increased by (1) increasing the sodium concentration of the amalgam, (2) decreasing the sodium hydroxide concentration of the electrolyte, (3) increasing the temperature.

The anode polarization e_2 is a small potential caused by the slow diffusion of sodium to the amalgam surface and sodium ions away from it. This potential is decreased by (1) increasing the temperature, (2) decreasing the sodium hydroxide concentration, (3) decreasing the current density.

Potential required to overcome the resistance of the electrolyte e_3 increases directly as the distance between the anode and cathode and inversely as the cross section of the electrolyte. It is at a minimum for approximately 19 per cent caustic solution. It decreases with increasing temperature.

Hydrogen overvoltage, e_4, is characteristic of an electrode surface. For a given surface, it is decreased by (1) increasing the temperature, (2) decreasing the current density.

Surface overvoltage after long continued electrolysis is the important value. Very minute impurities in the electrolyte deposit on the cathode. A metallic cathode, such as one of iron, must be placed an appreciable distance away from the amalgam surface or it will rapidly become covered with mercury and become inoperative. Cast iron shows the least tendency of the common metals to become coated, but it fails eventually and must be replaced. The surface activity may be renewed by allowing it to rust. Graphite has a higher overvoltage than some of the metals, but it can touch the amalgam without being coated by mercury or losing its reactive surface. One type of cathode is made of pieces of graphite dipping into the amalgam. Both electrolyte and metallic resistances are then at a minimum.

Hydrogen discharge potential e_5 is the equilibrium voltage between the solution and the electrode. It may be calculated from the activity of the hydroxyl ion in solution. It is decreased by (1) increasing the temperature, (2) diluting the sodium hydroxide solution.

Potential required to overcome the metallic resistance e_6 is the product of the current and the sum of the resistances through the amalgam sheet, the cathode, and any contact resistance between the two.

Practical considerations require a concentrated sodium hydroxide solution and a dilute amalgam so the cell must be designed with the opposing potentials at a minimum. This is obtained by (1) exposing a large surface to decrease the anode and cathode current densities, (2) placing the two electrodes as close as possible, (3) choosing a cathode with a low overvoltage, (4) operating at a high temperature.

Temperature. The solubility of chlorine in the electrolyte is lowered by increased temperature, but the velocity of reaction of hypochlorite formation is raised. Hydrogen overvoltage at metal electrodes and OH^- ion overvoltage at graphite vary inversely with temperature. In mercury cells the decomposition rate of the sodium amalgam varies directly with temperature. Salt solubility is fairly constant over a wide temperature range.

A summary of the desirable conditions for salt electrolysis is given in Table 59. Commercial cells incorporate these conditions in their design and operation, but the methods of taking care of all factors may be quite dissimilar.

Classes of Cells. Chlorine cells can be divided into a number of different classes according to the way their designs achieve

TABLE 59. DESIRABLE CONDITIONS FOR SALT ELECTROLYSIS

	Diaphragm Cells.	Mercury Cells

I. Anodes	1. Resistant to chlorine attack
	2. Graphite
	    a. Maximum density
	    b. Homogeneity
	    c. Minimum porosity
	    d. High mechanical strength
	    e. Resistant to disintegration
	        and oxidation	

II. Cathodes	3. Inexpensive 4. Low hydrogen overvoltage 5. Resistant to attack by cathode products	
III. Effective separation of anode and cathode products by:	Diaphragms 1. Minimum resistance electrically and hydraulically 2. Maintenance of porosity 3. Chemical inertness 4. Ease of mechanical replacement	Liquid intermediary electrode 1. Effective circulation 2. High hydrogen overvoltage 3. Low sodium overvoltage by regulation of alloy composition 4. Minimum mechanical and chemical loss from cell
IV. Electrolyte	1. Purified solutions free of heavy metal ions or ions forming insoluble hydroxides 2. Saturated brine solutions for low chlorine solubility	
	3. Circulation to minimize hydroxyl ion migration and diffusion of electrode products	3. Hydroxyl ion migration prevented by intermediate liquid electrode

certain desired results. Effective separation of electrode products is attempted by moving electrolytes, static electrolytes with diaphragms, circulating cathodes, as well as by moving electrolytes with a wide variety of diaphragm designs. Circulation of electrolytes with effective electrode-product separation by diaphragms minimizes all losses.

Diaphragm cells all produce cathode liquors containing more salt than alkali, an average composition being 110 to 120 g NaOH per liter and 140 to 170 g NaCl per liter, so that the caustic is not free of salt. Mercury cells are capable of much higher concentrations of salt-free caustic.

TABLE 60. CLASSIFICATION OF CELLS

I. Circulating intermediate electrode
  1. Mercury
    a. Castner
    b. Sorensen
    c. Rectangular horizontal
    d. Mathieson
    e. Vertical
  2. Fused lead
    a. Acker
II. Moving electrolyte
  1. Bell jar
III. Diaphragm cells with stationary electrolyte
  1. Griesheim
IV. Diaphragm cells with circulating electrolyte
  1. Horizontal submerged diaphragm
    a. LeSueur
  2. Vertical submerged diaphragms
    a. Macdonald
    b. Basle
    c. Townsend
    d. Pomilio
    e. Hooker
  3. Vertical free diaphragms, rectangular cell shape
    a. Hargreaves-Bird
    b. Allen-Moore
    c. Buck-McRae
    d. Double diaphragm
    e. Nelson
  4. Vertical free diaphragms, cylindrical cell shape
    a. Gibbs
    b. Vorce
    c. Wheeler
    d. Tucker-Windecker

The various commercial cells are classified and designated by the names of their proposers, designers, or manufacturers. They will be individually discussed in the order shown in Table 60.

MERCURY CELLS

Mercury cells may be built in small (1,000 amp) to very large sizes to 30,000 or even as high as 50,000 amp or more per unit. Purified saturated brine is fed to the cells and commonly circulated through them with a reduction in salt concentration. Brine is resaturated for another cycle. Each unit consists of two sections: one which is closed and has a chlorine outlet, graphite anodes, and a mercury cathode; and a second, the denuder section, containing a mercury amalgam anode and iron cathodes, circulation of the mercury between the first and the second sections constituting the electrical connection. The current efficiencies depend upon the concentration of the amalgam formed in the first section and the effectiveness of the circulation of the amalgam. Current densities in mercury cells are considerably higher than in diaphragm units, being of the order of 1 amp or more per square inch of anode surface.

The first type of mercury cell, devised by Castner, of a size suitable for the manufacture of pure caustic soda and chlorine, consisted of a stationary, thick cast-iron base in which cylinders were bored for the ram pumps used to circulate the amalgam. There were two anode chambers for electrolysis of brine and an intermediate chamber for production of caustic soda by decomposition of the amalgam. This cell worked well for a time but always failed due to seizure of the ram pumps which was caused by the growth of a deposit of caustic soda.

It is interesting to note that this pilot plant was the forerunner of the modern cell with metal base.

Castner surmounted the difficulty of pumping mercury by the use of a rocking cell, and the first battery of these was erected at Oldbury in England in August, 1894, for demonstration purposes. A similar demonstration plant was built in 1895 in Saltville, Va., and the process was accepted by Mathieson Alkali Company at the end of March, 1896.

Thereafter the Castner-Kellner Alkali Company started production in the new works at Weston Point, Runcorn, in March, 1897.

The Mathieson Alkali Works at Niagara Falls commenced production, using rocking cells, in 1897.

Working independently, Kellner had developed a stationary cell, similar in principle to Castner's cell but using compressed air to pump the mercury. Castner used carbon anodes whereas Kellner used platinum.

The patents of Castner were acquired by the Aluminum Company of Oldbury, and in 1895 this company concluded an agreement with Solvay & Company of Brussels who, in the meantime, had become owners of the Kellner patents. It was in one of the Solvay works that the first long cell was developed by A. Brichaux and H. Wilsing. This cell comprised a metal trough lined with concrete. It was equipped with platinum anodes and with a scoop wheel for pumping the mercury. The first patents for the circulation of mercury were taken out in 1898.

The replacement of rocking cells by the long cell at the Castner-Kellner Works began in 1902 immediately the prototype had been approved. This cell, made of precast concrete in sections, was provided with graphite anodes and with an Archimedean screw pump for the mercury. The current was supplied to the cathode through bolts with flat tops.

Subsequently, replacement of concrete by the more resistant ebonite-lined steel took place. The object to be achieved was a reduction to the minimum of debris in the cell. This form of construction was a feature of mercury cell practice in Germany, where the process was adopted on a large scale after 1933.

The operation of the process for electrolysis of brine by the mercury cell has its difficulties, the chief of which is to avoid decomposition of sodium amalgam in the brine cell, since the hydrogen content of the chlorine is governed by this. Another important factor is the loss of efficiency by recombination of sodium in the amalgam with chlorine dissolved in the brine. In general, the higher the cathode current density, the more likelihood there will be of a higher current efficiency.

The decomposition of sodium amalgam to produce caustic soda liquor is effected in a short-circuited primary cell. At first this was achieved using cast-iron grids as cathode to the sodium amalgam anode. Amalgamation of the cast-iron grids was a nuisance since the cathode was thereby rendered ineffective. Graphite has replaced cast iron and other alloys for this pur-

pose, with a consequent advantage in the production of 50 per cent or stronger caustic soda liquor direct.

In the cells in use in the United States, the mercury is usually in the horizontal layer. First cost, as the result of the quantity of mercury employed per cell, is high. The current efficiencies are of the same order as the diaphragm units. The voltages tend to be higher than diaphragm cells for small units, but the same does not hold true for large capacities. Evaporation costs
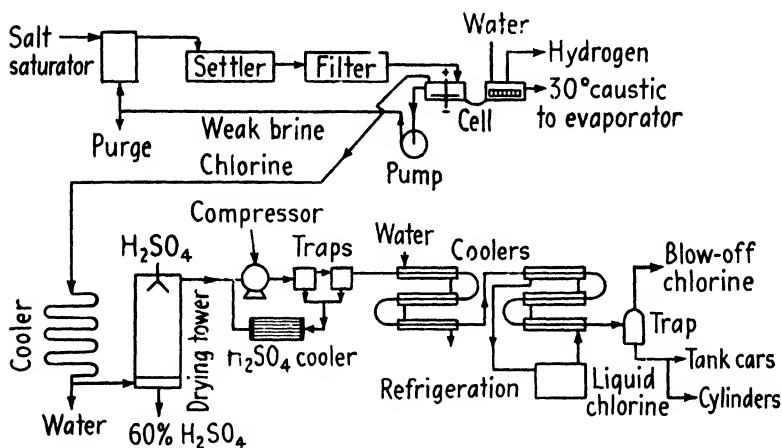
Salt - 1.5 to 1.8 tons   Electricity - 3,250 kwhr ⎫ Per ton caustic soda
Sulfuric acid (66° Be) - 25 lb   Refrigeration - 0.9 tons ⎬ plus 1,750 lb. chlorine and
Steam - 6,000 lb   Graphite - 7-10 lb ⎭ 87,500 cu ft hydrogen

FIG. 102. Flow sheet of the mercury cell process for alkali and chlorine.

of alkali liquors are markedly cut down, inasmuch as the cells can produce caustic solutions of 50 per cent concentration which may be shipped directly. The caustic is salt free, an advantage in connection with viscose rayon manufacture. Commonly the circulation of the mercury is by mechanical means, such as paddle wheels, various forms of pumps, and screw elevators, in contrast to the rocking-cell idea of the earliest units.

A flow sheet of the mercury cell process is shown in Fig. 102. Filtered saturated brine is fed to the brine cell at approximately 1 ml per min per amp of cell current although no appreciable change in operation occurs until the rate is reduced to 0.3 ml per min per amp. Brine flows out of the cell and is resaturated

by the addition of solid salt. The resaturated brine is settled and filtered before returning to the cell.

Energy efficiencies are of the order of 50 to 60 per cent. Anode consumption when graphite anodes are used is of the order of 6 to 7 lb per ton of chlorine. Mercury losses are small, being of the order of 0.15 to 0.25 lb per ton of caustic. When calculated on the basis of the yearly output per cell, the necessary annual replacement of mercury is less than 2 per cent to cover all losses.

In commercial cells the total voltage across the cell—made up of the anode potential, chlorine overvoltage, voltage drop

Chlorine   *Brine* *Water*   *Hydrogen*

Brine   *Caustic soda*

Mercury   *Partition*
        Brine cell   *Denuding cell*
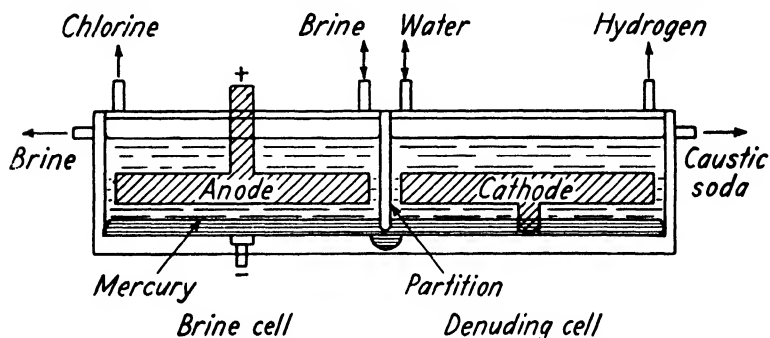
Fig. 103.   Mercury cathode type of alkali and chlorine cell.

through the electrolyte, film resistances, and cathodic potentials —is 3.85 to 4.3 volts, depending upon the design and current capacity of the unit. The electrodes are usually placed very close together.

In the United States the mercury cell has assumed several commercial forms. The original mercury cell is credited to Castner, while the Whiting and Sorensen may be considered as modifications.

Castner Cell. Figure 103 shows the construction of Castner cells diagrammatically. It consists of two compartments divided by a partition of insulating material that is not affected by chlorine or caustic soda. Under the partition there is a groove so that when mercury is placed on the bottom of the cell a liquid seal is formed which permits the free passage of the mercury but separates the other fluids. The mercury must be circulated from one cell to the other.

The brine cell is constructed of an insulating material, such as

concrete, that is inert to chlorine. Mercury on the bottom of the cell is connected to the negative pole of a current source by means of a bolt passing through the cell bottom. The positive pole is connected to an anode of graphite supported from the cell cover so that it is near the mercury surface. Nearly saturated brine is fed in at one end of the cell and partially depleted brine is removed at the other end. A chlorine outlet is provided:

(a) Original Castner

(b) Castner double-circuit

(c) Castner-Kellner shunt

(d) Kellner short-circuit
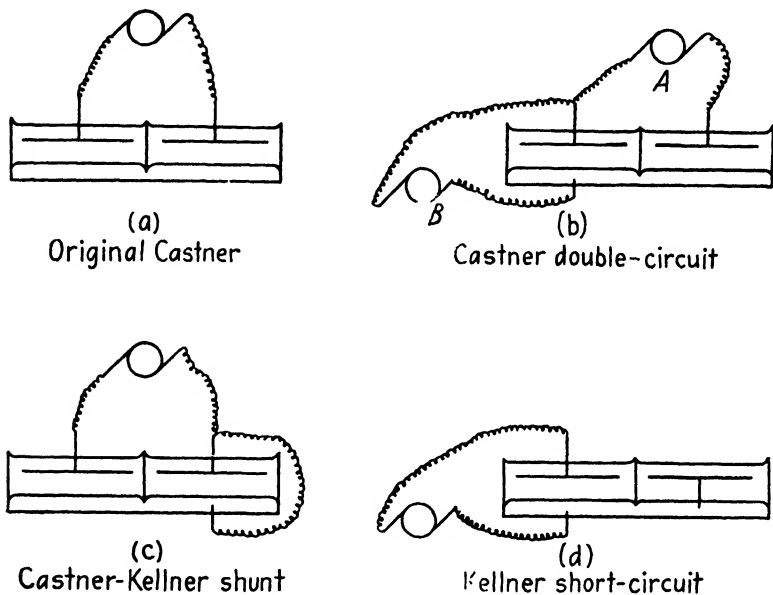
FIG. 104. Proposed short-circuited cathode systems.

The denuding cell can be made of either iron or concrete. The cathode is short-circuited to the sodium amalgam. Other external electrical connections proposed and used are shown in Fig. 104. A graphite cathode can be placed in the amalgam as its surface does not amalgamate. The cathode is covered by a solution of sodium hydroxide. Water is fed continuously into the cell, and pure concentrated caustic soda overflows.

In Castner's "rocking cell" the whole cell is tilted to make the amalgam flow back and forth. In the "stationary cell" the mercury is moved by a pump from the low end of a sloping denuding cell to the high end of a sloping brine cell.

The Whiting cell had as its feature an automatic intermittent

removal of the amalgam from the electrolyzer.[3]   It was at one time used at one paper plant in the United States.

Sorensen Cell.   A typical installation of the Sorensen cell is shown in Fig. 105, and diagrammatically illustrated in Fig. 106. The structural materials are concrete and steel; the anodes are graphite plates arranged with their surfaces parallel to the mercury surface.   The cell consists of an electrolyzer compart-
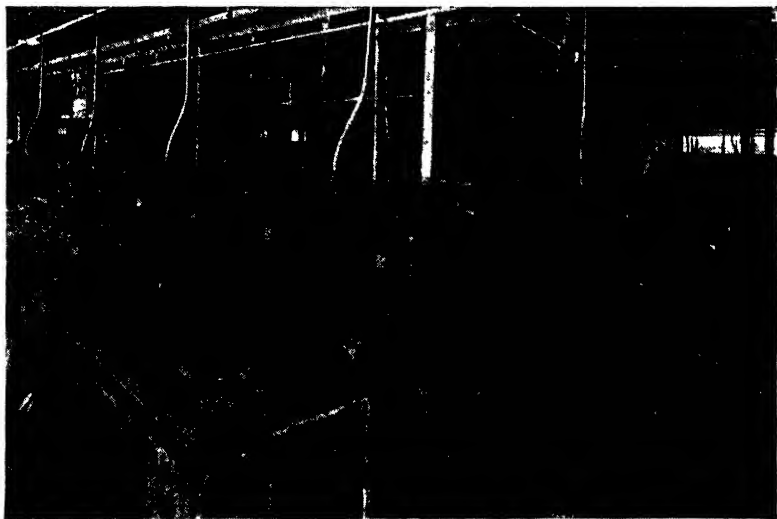
Fig. 105.   An installation of Sorensen cells.   (*Oxford Paper Company.*)

ment or box and a denuder compartment or box, the mercury being mechanically circulated by means of a cup wheel which feeds the mercury into the electrolyzer compartment, the bottom of which is at a higher level than that of the denuder.   Connection between the electrolyzer and the denuder is through a channel at one end of the cell, while the mechanical handling of the mercury is at the other.   Instead of traveling from side to side as in the Castner cell, the mercury travels from one end of the electrolyzer to the other, through to the denuder and from one end of the denuder to the other, and then is picked up from the low point of the denuder and raised to the high point of the electrolyzer.   The feed inlet is located at the top of the cell, the chlorine outlet at the side; the hydrogen outlet is at the top of,

[3] WHITING, J., *Trans. Am. Electrochem. Soc.*, **17**, 327 (1910).

and the cathode alkali outlet at the side of, the denuder compartment. The cathode is iron. See Table 61 for operating data.

Horizontal Cell. This cell is composed of a primary or electrolyzing section and a secondary or denuding portion. The electrolytic section consists of a long rectangular trough made of ebonited or rubber-covered steel. On the lower surface, in the
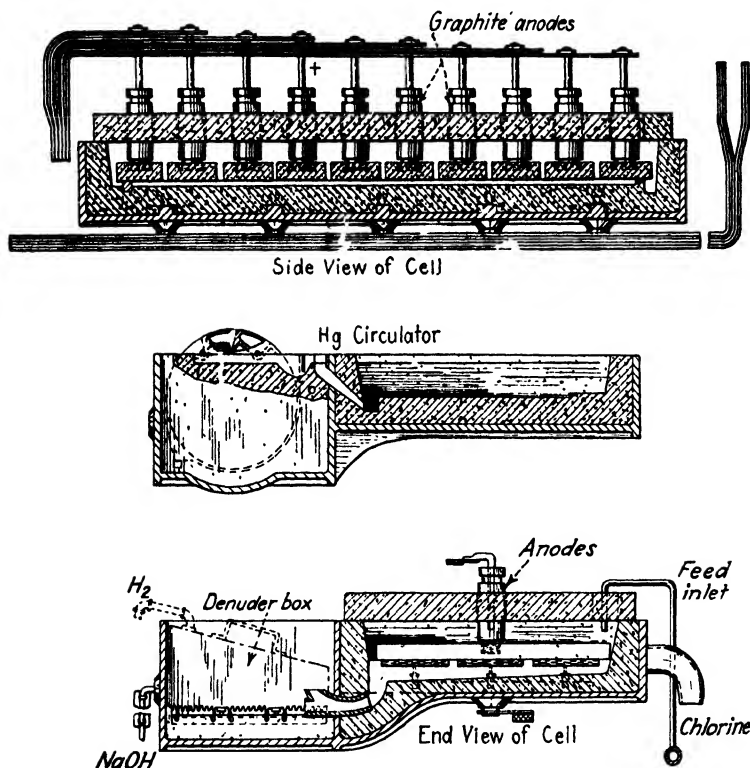
FIG. 106. Construction of the Sorensen cell.

ebonite lining, sockets are inserted. These sockets are in direct contact with a thin layer of mercury covering the bottom and forming the negative pole of the cell. The cover of this element is made of chlorine-resisting material; through it run graphite rods which lead the current to the anodes. The latter are formed by horizontal graphite plates fixed at a very small distance from the surface of the mercury.

The secondary element is formed by a rectangular steel trough of the same length as the primary cell. The lower surface is covered on all its length with graphite grids which are in direct contact with the iron. All the upper part of the secondary element is covered with iron lids with water closing devices.

The electrolytic and the denuder sections or elements are connected on one side by a cast-iron casing, in which is a pump for the circulation of the mercury. On the other side is a device through which the mercury flows from the primary to the secondary element. Both elements have a slight slope, in opposite directions, assuring good circulation of the mercury. Cells are built in capacities of 4,000 to 30,000 amp, although this is not the structural limit. Dangers from explosions which were a hazard in the old types of mercury cells are eliminated by automatic light and sound signals.

In starting the cells, the mercury pump is put into operation, the brine cock opened, the secondary element filled with water containing sufficient alkali to be conductive, and current is applied to the cells which are then built up to full load. When the caustic solution in the denuder section has reached the desired concentration, the distilled water line is opened and the flow regulated so that enough distilled water is introduced to balance the outflowing caustic at the other end of the cell. The air in the chlorine lines is expelled by means of chlorine generated in the electrolysis section and the air in the hydrogen line is displaced by hydrogen evolved in the denuder section.

The horizontal rectangular mercury cell in comparison with the diaphragm cells will operate under considerable variation of the current load. Anode life is about 2 years. Anodes are consumed at a rate of the order of 3.2 kg per 1,000 kg of chlorine, or 0.0032 lb of graphite per pound of chlorine. Mercury consumption is of the order of 75 to 100 g per 1,000 kg of NaOH, or 0.0001 lb per lb of caustic. The chlorine concentration is of the order of 96 to 98.5 per cent, containing from 0 to 0.5 per cent hydrogen.

Figure 107 diagrammatically illustrates the horizontal mercury cell. A typical plant is shown in Fig. 108 where the relation of the electrolyzing and denuder sections as well as the mercury circulating pumps at the end of the cell is shown. Operating data on the cell are given in Table 61.

Mathieson Cell. An American version of the horizontal cell which was largely developed in Europe is that of Mathieson Alkali Works, illustrated diagrammatically in Fig. 109. The operating details are given in Table 61.
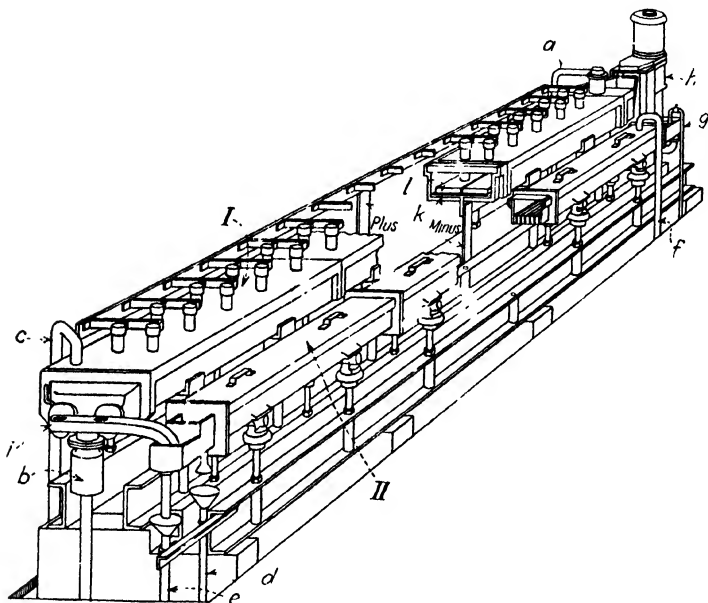
Fɪɢ. 107. Diagrammatic representation of horizontal mercury cell.

At (a) the electrolyte (brine) enters the electrolytic compartment (I) of the cells and leaves it at (b). The mercury is kept in circulation by the conveying device (h); it flows in the electrolytic compartment in the same direction as the electrolyte. The mercury charged with sodium flows over through the gutter (i) into the amalgam decomposition compartment (II). Here the amalgam is decomposed giving mercury, caustic soda, and hydrogen. The water necessary for decomposition enters the decomposition compartment at (g). The concentrated lye runs out at (d). Hydrogen leaves the decomposition compartment at (f). The chlorine gas leaves the electrolytic compartment at (c). An outlet for impurities is at (e). The electric current is led into the electrolytic compartment by the anodes (l) and out by the cathode (k).

DeNora Cell. This cell is of the horizontal mercury type with a vertical decomposer. The cell feature is the lining of natural siliceous stone in the electrolysis chamber. Operating characteristics are similar to the horizontal cell. Floor space for a 30,000-amp unit without aisles is 52 by 3 ft, with an operating voltage of 4.5.

FIG. 108. Horizontal mercury cells showing electrolyzer and denuder sections with mercury circulating pump.

AMALGAM DECOMPOSER
Water inlet to pump
Signal lamp
Pump motor
AMALGAM PUMP
Brine outlet ----OUTLET END BOX
Anode cables
Anode support plate
Cover clamp and pad
Cover
Anode gas seal ring
Anode support clips
ELECTROLYZER Anode gas seal
Cover gasket
Anode lead-in and insulator
Graphite anode
Cell bed
Side angle gasket
Side angles
INLET END BOX

Auxiliary switch pump alarm system
Wash water overflow from pump
Mercury return to inlet end box
Water inlet to amalgam decomposer
Caustic and hydrogen outlet
Switch control lever
Anode bus bar
Short circuiting switch
Cathode bus
Insulator
Concrete curb around floor opening
Rotameter
Chlorine outlet
Brine inlet control valve

FIG. 109. Mathieson cell with amalgam decomposer.

Vertical Mercury Cell. This type has been intensively studied in Germany because it has large capacity per unit of floor space. Diagrammatically it is shown in Fig. 110. A 24,000-amp cell is shown in Fig. 111, while operating data are given in Table 61.

In the Ludwigshafen design the cell consists of a steel drum or rotor 1.97 ft (0.60 m) in diameter by about 1.64 ft (0.50 m) in width mounted on a horizontal shaft. This drum carries five circular cathode plates at right angles to its axis, each plate being 6.07 ft (1.85 m) in diameter, about 0.79 in. (2 cm) thick,
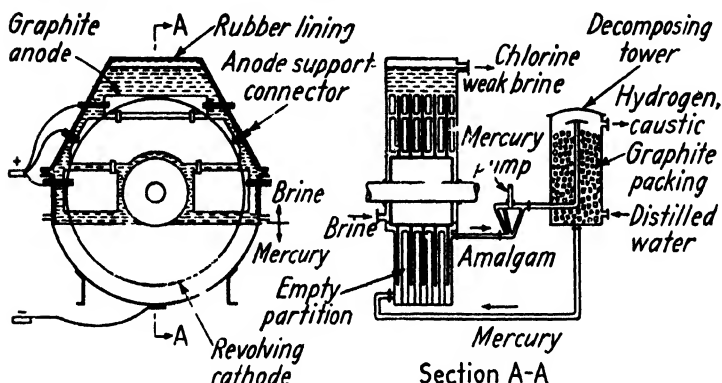
Fig. 110. Vertical chlorine cell, Ludwigshafen design. Sodium is carried out of brine electrolysis zone by mercury-coated cathodes; amalgam dissolves in mercury bath and goes to decomposer for removal of sodium with water. The cycle is continuous.

and spaced equidistant from the others. The drum and its plates are enclosed in a steel housing which is split horizontally into three sections. These are flanged and bolted together. The top section has sloping sides; the middle section is roughly square sided; and the bottom section is curved to conform to the circular cathode plates. The middle section extends from about 6.3 in. (16 cm) above the center of the rotor shaft to about 7.9 in. (20 cm) below it. All but the bottom section are rubber-lined. The cathode assembly is rotated at about 7 rpm. Graphite anodes are supported from the cell housing through connectors. Anode assemblies are split horizontally and a 0.79-in. (20-mm) space left to facilitate circulation of the brine.

Approximately 1,300 kg of mercury fills the bottom of the cell housing to a height about 0.79 in. (2 cm) above the bottom of the rotor.

Purified and nearly saturated hot brine (70°C, 310 g per liter) is fed in through the cell housing at one end just above the surface of the mercury. This brine fills the housing above the mercury to within about 1.57 in. (4 cm) of the top where it overflows, after depletion of its NaCl content to about 260 g per liter. Chlorine gas also passes out through this overflow pipe and is later separated from the weak brine.
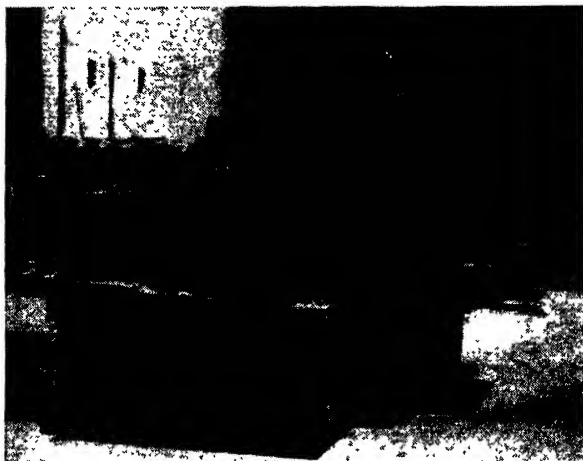
FIG. 111. Vertical rotary mercury chlorine cell in I. G. Farbenindustrie plant, Ludwigshafen. (*Chemical Engineering.*)

German Practice. Table 62[4] gives a cross section of German chlorine and caustic practice covering six plants, two of which had both mercury and diaphragm cells. Floor space per short ton of chlorine for mercury cells was from 440 to 640 sq ft. The pounds of mercury in the cell per pound of chlorine per day was stated to be as low as 1.4 to as high as 2.4. The mercury losses varied widely. The power requirements were of the order of 1.65 to 1.85 kwhr per lb of chlorine.

Acker Cell. The Acker cell employed a fused lead cathode which was circulated between a decomposing chamber and the cell proper. The electrolyte was fused NaCl. The caustic produced

[4] Technical investigation reports as interpreted by Ralph M. Hunter, Dow Chemical Company.

TABLE 61. ELECTROLYTIC CHLORINE AND CAUSTIC—MERCURY CELLS

	Sorensen	Castner	Bitterfeld	Horizontal rectangular	Matheson 12,000 amp	Matheson 15,000 amp	Vertical
Cell shape.....	Rectangular	Rectangular	Rectangular	Rectangular	Rectangular		Cylindrical
Voltage across cell	4 2		4 5-5 0	3 85-4 0	4 25		3 75-4 7
Current per cell, amp	1,300		15,000	3 500-15,000	12,000	15,000	24,000-40,000
C.d., anode, amp/sq in	0 80		1 4-2 0	1 0 -1 68	2 4		1 05
C.d., cathode, amp/sq in	0 80		1	0 97-1 61			
Current efficiency of cell, %	90-95		95 0	94-96	95		92-93
Energy efficiency of cell, %	48-52		50-60	50-60			50-58
Lb NaOH per kwhr	0 70		0 6-0 66	0 68-0 75	0 73		0 58-0 65
Lb Cl₂ per kwhr	0 63		0 54-0 6	0 6-0 67	0 6s		0 53-0 59
Tons salt per ton caustic			1 7		1 7		1 7
Lb Hg per ton caustic			0 36		0 5		0 5-1 25
Lb graphite per ton Cl₂			6 7		? 4		9-13
Lb graphite per ton caustic			6		7.5		8 1-12
Anode material	Graphite		Graphite	Graphite	Graphite		Graphite
Cathode material	Mercury		Mercury	Mercury	Mercury		Amalgamated steel
Anode life, days	600		225		?10		
Average operating period of cell, days	300		200		210		
Raw material	NaCl		Brine	NaCl,300-315g/l	NaCl		NaCl
Concentration of cathode alkali	Up to 50%	30-50%	Up to 50%	350-650 g/l	Up to 50%		50-70%
Size anode	9 anodes, 20" × 9" × 2"		2½" × 7" × 25"	16 anodes, 1½" × 6" × 18"	16 anodes, 17¾" × 2½" × 17" × 2½"	20 anodes, 17¾" × 17" × 2½"	
Size cathode	Surface of mercury approximately the same as anode		23" × 26'	28' × 2'	28' × 2'	34' × 2'	
Salt concentration, inlet, g/l			310	310	310		310
Salt concentration, outlet, g/l			220-270	240-250	260		260
Hydrogen in chlorine, %			0 5-1	0 5	0 5-1 0		1 6
CO₂ in chlorine, %			1 -1 5	1	0 5		1
Size of cell, external measurements	50" × 6'0" × 1'0"		23" × 26'	28'8" × 23"	28'8" × 23"	34'6½" × 23"	6.1' diam.

TABLE 62. SUMMARY OF CHLORINE PLANTS IN GERMANY

(Six plants, totaling 530 tons of chlorine per day)

	Place and company							
	Mercury cells						Billiter diaphragm cells	
	Burghausen, Wacker	Gendorf, I.G.	Bitterfeld, I.G.	Zscherndorf, Kali Chem.	Osternienberg, Solvay	Gersthofen, I.G.	Bitterfeld, I.G.	Burghausen, Wacker
Production, lb per day	49,000	250,000	200,000	85,000	66,000	140,000	240,000	39,000
Amp per cell	15,000	16,500	15,000	19,500	10,000	14,500	10,000	6,000
Volts per cell	4.4–5.0	4.5–5.0	4.5–5 0	4.3–5 0	4.3	4.2–4.4	4.5	5.0
Ampere efficiency			95 0	96.0		95.0	94.0	
Kwhr/lb of chlorine	1.7	1.82	1 67–1.85	1 6–1 85	1 65	1.58	1.67	1.82
Lb of graphite per 2,000 lb Cl_2		6 0	6 7	8.0	7 5	5.8	9.0	
Man-hours per 2,000 lb of chlorine	2.6	2.7	3 0	1.9		4.3	3.2	2.4
Electrolyzer size	25″ × 36′	27″ × 23′	27″ × 26′	25″ × 40′	25″ × 40′	28″ × 20′	10′ × 18′	4′ × 18′
Bldg. for cells, sq ft per 2,000 lb Cl_2	640	460	560	440		600	1,200	
Amp c.d. per sq in. anode	2 1	2.2	1 4–2 0	1 75	2 1	2 4	1.25	0.9
Lb of Hg in cell per lb of Cl_2	1.82		1 8	1 78	2 7	1 42		
Mercury loss per year, %	7	4–6	4	< 1				

was colored as the result of contamination by metallic salts or oxides, particularly iron. The cell is described in connection with fused electrolytes. The chlorine resulting from the cell was hot and dry and needed to be cooled for conversion into liquid chlorine.

CELLS WITH MOVING ELECTROLYTE

In cells with moving electrolytes and no diaphragm, alkali and hydrogen are formed in the electrolysis chamber; the effects of diffusion and ionic migration are counteracted by a flow of electrolyte arranged to oppose the diffusion of alkali and the migration of OH⁻ ions toward the anode. One type is the bell jar or gravity cell of which the original and largest installation was at Aussig in Bohemia. This design finds no application in the United States. It is shown diagrammatically in Fig. 112. A bell jar, consisting of a nonconducting and nonporous material, is inverted in a vessel containing the NaCl electrolyte, while outside the bell there is a ring-shaped iron cathode. The graphite anode

FIG. 112. Bell-jar cell.

is inside the bell. Brine feed is through the top of the bell, past the anode. The bell also contains a chlorine outlet. An alkali boundary, more or less sharp in nature, exists. A neutral layer is formed as the result of downward flow of brine solution at a definite level between the bottom edge of the bell jar and the lower surface of the anode. This downward travel of the electrolyte reduces OH⁻ ion migration and diffusion. Commercially the cells are small in size. It is difficult to maintain the alkali-salt solution boundary.
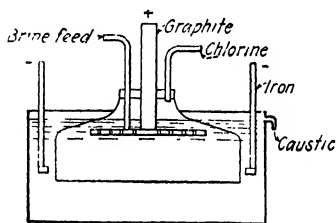
The bell jars are constructed of sheet iron lined with cement. The anodes are of graphite. Single bell jars take 20 to 30 amp at a current density of about 0.2 amp per sq in. (3 amp per dm²), a number of them being assembled into a complete cell taking 500 amp. Current efficiency is about 90 per cent when saturated brine solutions are used, and cathode liquors run 100 to 120 g NaOH per liter.

In continental Europe a number of modifications of the bell-

jar cell have been brought into existence, such as the Billiter-Leykam[5] and the Carmichael cells.[6]

DIAPHRAGM CELLS

Griesheim Cell. An example of diaphragm cells in which stationary electrolytes are employed is the Griesheim Electron cell.[7] Here the disturbing effects of convection currents and gas
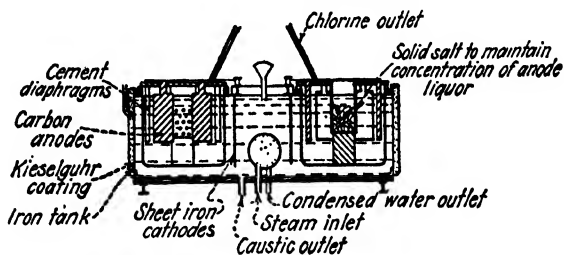
FIG. 113. Griesheim Electron cell.

evolution are avoided, but migration of OH^- ions toward the anode is not prevented. The cell is relatively inefficient but is simple, cheap, and easy to operate. The unit is shown diagrammatically in Fig. 113. It consists of a rectangular iron tank coated with a layer of thermal insulator. The tank serves as cathode and contains 12 anode compartments made of portland cement diaphragms suspended on an iron frame. Each anode compartment contains 6 carbon or magnetite anodes cemented on the cover and parallel to the sides of the box. The anode compartments have chlorine outlets and have inserted in their center a well made of glazed porcelain which is kept filled with solid salt. The porcelain is pervious to the action of the electrolyte which dissolves the salt to maintain its saturated condition. In the center of the tank heating pipes are placed and auxiliary sheet-iron cathodes suspended vertically. Operating details are given in Table 63.

⁵ FOERSTER, F., "Elektrochemie wässeriger Lösungen," p. 749, J. A. Barth, Leipzig, 1923; NUSSBAUM, J., article in Askenasy's "Technische Elektrochemie," Vol. II, p. 233, 1916.

⁶ *Z. Elektrochem.*, **1**, 213 (1894); HABER, F., *ibid.*, **9**, 366 (1903).

⁷ HÄUSSERMANN, C., *Dinglers Polytech. J.* (30) 315, 469 (1900); LEPSIUS, B., *Chem. Z.*, **33**, 299 (1909); BILLITER, J., "Die Elektrochemischen Verfahren," Vol. II, p. 166 (1911); NUSSBAUM, J., p. 180 of his article on diaphragm cells in Askenasy's "Technische Elektrochemie," Vol. II, 1916. The first two references describe the older form of the cell not here dealt with.

Cells with Circulating Electrolyte. The most widely used cells for salt electrolysis are those of the circulating electrolyte-diaphragm type. These are divided into rectangular and cylindrical forms. The anodes almost universally in use are of graphite, which is nonattackable by chlorine. Diaphragms may be arranged either horizontally or vertically, but in the United States at least the former is represented only by the LeSueur cell. In reference to the diaphragms the cells may be subdivided into two groups: (1) those in which the diaphragms and cathodes are completely submerged so that both sides of the cathode are covered with electrolyte; (2) those in which the electrolyte comes in contact with one face only of an unsubmerged diaphragm. The diaphragms, which are permeable, are arranged structurally in a number of ways.

With submerged diaphragms it is possible to a large degree to keep the cathodic and anodic products separate by maintaining a liquor level in the anode compartment higher than that in the cathode compartment, whereby a continuous flow results from the anode chamber to the cathode chamber. Osmosis of the cathode products as well as OH⁻ ion migration can occur through the diaphragm into the anode compartment. As a result of this, hypochlorite can form. It was formerly thought that submerged diaphragm cells tended to operate at low current efficiency. As the age of the diaphragm advances, it becomes less permeable and gradually more effective as an osmotic vehicle for the contamination of the anode compartment by the cathodic products.

With nonsubmerged diaphragms there is no large body of salt and caustic liquor present in the cathode compartment because the cathode liquor is withdrawn as fast as it is formed. Osmotic action and OH⁻ ion migration will thus be cut down to a minimum. Submerged diaphragm cells are represented in the commercial units of Pomilio and Hooker.

The industrial cells of importance, employing free diaphragms, are the Hargreaves-Bird, the Allen-Moore, the Buck-McRae, the Larchar, the Nelson—all of which are rectangular cells employing unsubmerged diaphragms—and the cylindrical cells of Gibbs, Wheeler, Vorce, and Tucker-Windecker. The design, construction, and operation of each of these cells in their commercial forms will be discussed individually. As a link between the submerged and unsubmerged cathode cells, mention will be made

of the Macdonald and the Basle cells, although neither is of importance in the United States. In general, however, discussion will be limited to cells which have achieved commercial importance. A number of designs, although of interest because of unusual features, are omitted. Their application never reached the commercial stage or, having reached it, did not persist.

With the exception of the Hooker and the Dow cells, American units were of lower amperage than European counterparts. German practice favored mercury cells replacing Billiter dia-
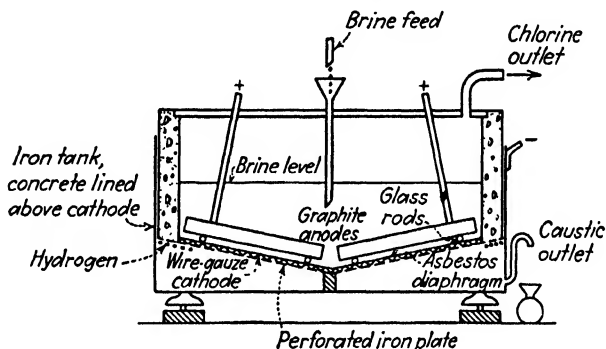
FIG. 114. LeSueur chlorine-caustic cell. (*Brown Company.*)

phragm units in many cases. Billiter cells remained in sufficient number to warrant description and are therefore included.

LeSueur Cell. The first commercial electrolytic caustic plant in the United States employed a horizontal submerged diaphragm cell designed by LeSueur.[8] An iron-wire screen cathode was supported by a perforated metal plate, while the asbestos paper diaphragm was, in turn, supported by the cathode. Originally the anodes were massive sections of retort carbon, but in later years electric furnace graphite was substituted. The tank for the cell was of iron, concrete lined. The cathodes made contact with the walls of the tank, and the external electrical connection was to the tank sides. · The cell is illustrated diagrammatically in Fig. 114, and operating details are given in Table 63.

Submerged Cathode Cells. Although unimportant in the United States, submerged cathode cells should be mentioned. The link between the submerged and unsubmerged is furnished

[8] LeSueur, E. A., *Trans. Electrochem. Soc.*, **63**, 187 (1933).

by the Macdonald cell, now obsolete, in which two perforated metal cathode plates supported asbestos diaphragms and divided the cell into a middle anode compartment and two outer cathode sections. Graphite anode blocks with lead lugs were suspended from an earthenware cover on an earthenware box. The diaphragm was held in place by masses of concrete in the bottom and ends of the anode compartment. In operation the liquors in the anode and cathode compartments were brought to the same level, brine being introduced into the anode compartment. The cell gave many operating troubles and had excessive upkeep as well as low amperage efficiency.
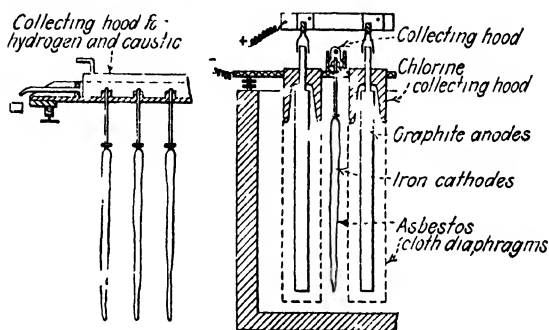
FIG. 115. Basle cell.

Basle Cell. The Basle cell of the Bussi plant of the Società Italiana di Elettrochimica features submerged cathodes and an individual diaphragm for each anode and cathode. The mechanism used to circulate the electrolyte from anode toward cathode is of interest. Both the graphite anodes and the iron cathodes are surrounded by asbestos bag diaphragms. Hydrogen generated at the cathode inside the bag carries the cathode products up through the short iron tubes into gutters on the top of the cell, the gutters being covered by a collecting hood. Chlorine is taken off at the top of each anode through nonconducting collecting bells. A constant level brine feed is used. The largest unit takes about 7,500 amp and produces 11 to 13 per cent NaOH, 98 per cent chlorine, at a current efficiency of 90 to 92 per cent and a voltage of 3.3 to 4.5 at 40 to 50°C. The construction of the cell is shown in Fig. 115.

Townsend Cell. The Townsend cell is rectangular in shape, containing one anode and two cathode compartments. The

anode space is formed between a lid or cover and two vertical diaphragms on the side of the nonconducting concrete body made in the shape of a shallow U, so that this body forms the bottom and ends of the cell. Graphite anodes pass through the cover into the anode space. The diaphragms are in close contact with perforated iron cathode plates which, in turn, are fastened to two iron sides bulging outward in the middle to form the cathode compartments. The cathode compartments contain kerosene oil. The anodes are large rectangular graphite blocks set end to end. In the early designs of the cell very little space
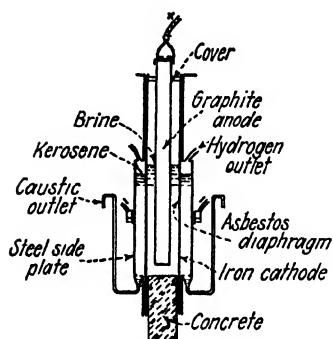
was allowed between adjacent anodes. The construction of the cell is shown in Fig. 116. Because of the difference in specific gravity between the saturated brine in the anode space and kerosene in the cathode compartment, there is a hydrostatic pressure from the anode chamber toward that of the cathode. This pressure is increased by maintenance of the anode liquor at a higher level than that in the cathode chamber.

Fig. 116.   Townsend cell.

Each drop of liquid, as soon as it traverses the diaphragm, runs through the perforations of the cathode plate and acquires a globular shape by capillary attraction on contact with the kerosene oil. This produces a rapid separation of the aqueous liquid so that each drop, as soon as it forms, detaches itself rapidly, sinks to the bottom of the oil to a small caustic pocket, where it may be drained off by adjustable goosenecks. Operating data on the cells as given by Hooker[9] are included in Table 63. The diaphragms in the Townsend cell consist of a woven sheet of asbestos cloth in which the pores are filled with a mixture of iron oxide, asbestos fiber, and colloidal iron hydroxide, the latter material functioning as a binder.

In plants employing the Townsend cell the salt liquors are continuously circulated, only part of the liquors entering the cell passing through the diaphragms. In the circulation cycle the liquor is resaturated after passing through the cells, which

[9] HOOKER, A. H., *Chem. & Met. Eng.*, **23**, 961 (1920).

it leaves at a specific gravity of 1.18 and has to be brought up rapidly to 1.2. Brine feed to the cell is purified of heavy metals and filtered. It is stated that percolation in the cell can be reduced to a point where cathode liquors containing as high as 250 g NaOH per liter may be produced, but that in practice it is advantageous to produce liquor containing 125 to 150 g NaOH per liter.

Giordani-Pomilio Cell. This cell is similar in appearance to the original flat-sided diaphragm cell, rectangular in shape, as

Fig. 117. Giordani-Pomilio cells of 3,000 amp. (*Celulosa Argentina.*)

patented by Hargreaves and Bird in the early nineties, and the American cell of Nelson and Moore. It differs from these, however, in that it resembles the Townsend cell in its use of the submerged cathode. The design includes an arrangement by which the height and, therefore, the hydraulic pressure of the liquid in the anode and cathode compartments of the cell may be varied according to the permeability of the diaphragm as it changes with age. The cells are thin and high, and the hydraulic levels in the anode and cathode chambers may differ by as much as a meter. The standard size cell is 3,000 amp, but units are built in ranges of 1,000 to 6,000. An operating cell room of 3,000-amp cells at Juan Ortiz, in the Argentine, is shown in

Fig. 117, and operating details on the cell are given in Table 63. Graphite consumption is stated to be 5 to 6 kg per metric ton of caustic produced.

Hooker Cell. Stuart, Lyster, and Murray[10] have described the Hooker cell which is cubical and employs a multiplicity of submerged diaphragms which are deposited in place. Figure 118 shows the cathode which is built of structural steel, with a freshly
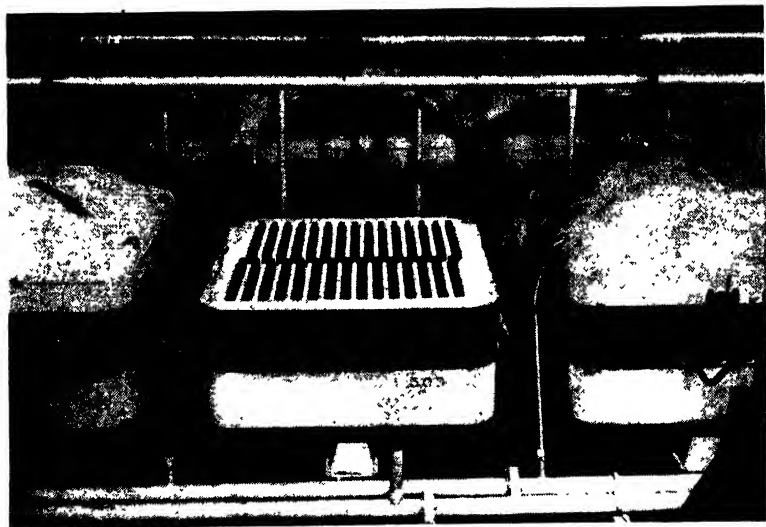
FIG. 118.   Hooker cell before putting on cover.   (*Chemical Engineering.*)

deposited diaphragm put in place by applying suction to the cathode frame and immersing the entire member in a suspension of asbestos. Figure 119 shows the essential members of the Hooker cell, where *A* is the concrete top through which the chlorine leaves and the brine enters, *B* the cathode assembly with the graphite anodes interspaced between the cathode sections, and *C* the concrete bottom of the cell. The anodes are parallel flat blades of graphite with their lower ends embedded in a lead slab resting upon the cell bottom, from which they project vertically upward. The cathode is formed within a flat rectangular frame of steel channels conforming to the concrete cell bottom, with rows of parallel cathode fingers projecting along

[10] STUART, K. E., LYSTER, T. L. B., and MURRAY, R. L., *Chem. & Met. Eng.*, **45**, 354 (1938).

two opposite sides and adapted to alternate with the anodes. Caustic liquor leaves the cell chamber through the framework of the cathode.

Stuart, Lyster, and Murray state that an alkaline chlorine cell should have electrode surface proportional to the cube of the linear dimension so that units might be built of any desired size; the electrode surface per square foot of floor space should be as great as possible; there should be no diaphragm edges within
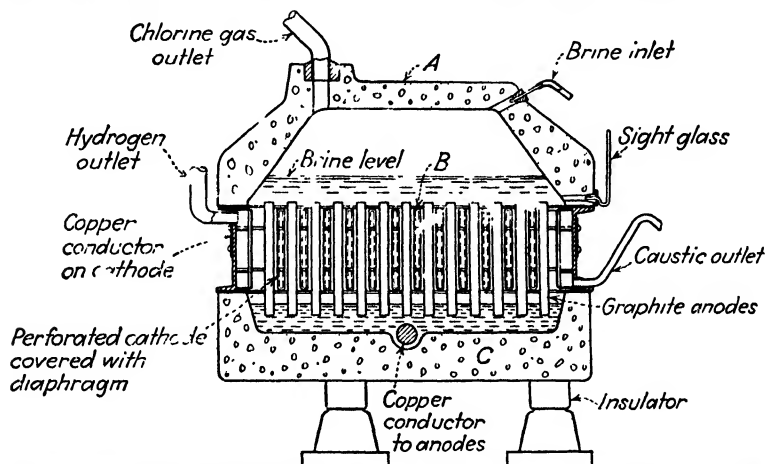
FIG. 119. Hooker Type "S" cell assembly. (*Chemical Engineering.*)

FIG. 120. Circuit of Type "S" cells in plant of the Hooker Electrochemical Company. (*Chemical Engineering.*)

the cell; and the most effective current density should be 60 to 70 amp per sq ft of anode surface.   An operating cell room of 6,000-amp cells is shown in Fig. 120; operating data are given in Table 63.

Hargreaves-Bird Cell.   The Hargreaves-Bird cell consists of an iron box, lined with brick and concrete and divided vertically along its length into three compartments by two cement-asbestos diaphragms made on heavy copper gauze which form the cathodes.   The middle compartment contains the graphite anodes.   Brine feed enters the cell at the bottom of this compartment and overflows at the top, a portion of the brine diffusing through the diaphragm and being electrolyzed.   There is no liquid in the cathode compartment except that which percolates through the diaphragm. Steam is introduced into the cathode compartment along with

Fig.   121.   **Hargreaves-Bird cell.**

Chlorine

Brine outlet

Graphite

Caustic

Steam + CO₂

Copper gauze

Asbestos

Brine feed

Fig. 122.   Hargreaves-Bird cell room.   (*West Virginia Pulp and Paper Company.*)

CO_2 which unites with the cathode alkali to form Na_2CO_3. The steam aids in keeping the diaphragms open. The cathode product of the cell is a mixture of $NaCl$ and Na_2CO_3. The cell is illustrated diagrammatically in Fig. 121, and a commercial plant is shown in Fig. 122. The commercial units show extremely long life. Operating data are given in Table 63. The cell finds application in connection with the pulp and paper industry. The outer cast-iron casing of the cell is lined with brick and cement which may be saturated with tar to prevent leakage.

Fig. 123. Allen-Moore cell.

Allen-Moore Cell. The Allen-Moore cell resembles the Townsend in certain structural features. The cell is built around a concrete shell with open sides and openings at the top through
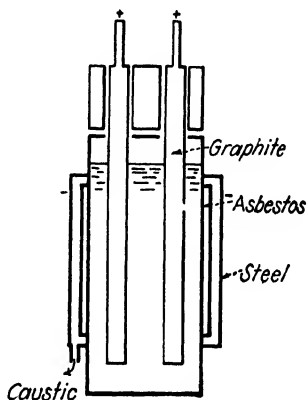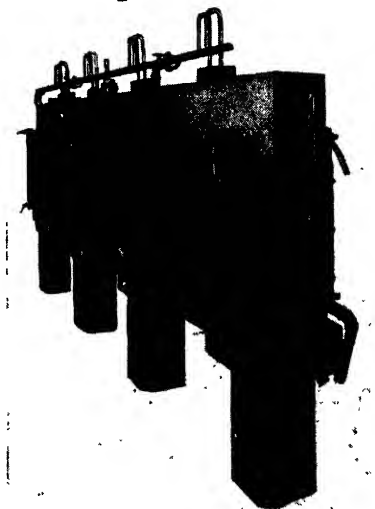
Fig. 124. Allen-Moore cell. (*Electron Chemical Company.*)

which the anodes are inserted. The construction can be seen from Figs. 123 and 124. Cathode compartments are bolted

externally on both sides of the shell over the openings.   These
carry the asbestos diaphragms backed by perforated steel sheets
which thus form the sides of the anode compartment, while the
cathode chamber itself is formed by the external steel casing.

   The KML Allen-Moore cell (Fig. 125) shows a modified con-
struction.   It consists of a steel tank forming the cathode com-
partment in which is suspended the multiple-compartment
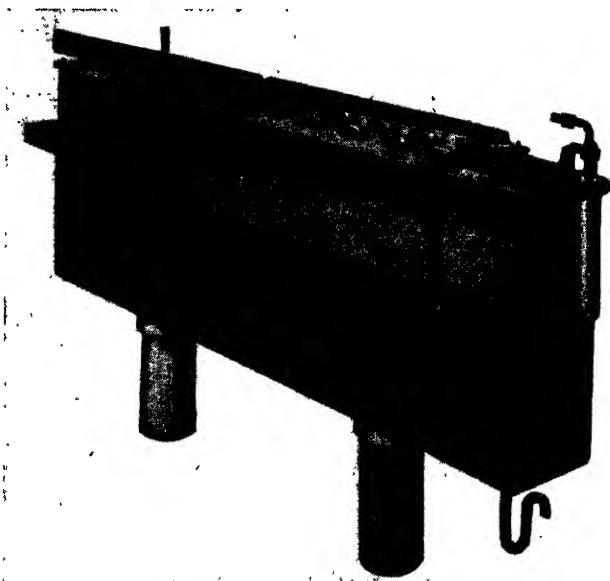
Fig. 125.   KML type of Allen-Moore cell.

cathode carrying the asbestos diaphragm.   Superimposed on
this tank and cathode is the concrete chlorine chamber through
which pass the graphite electrodes arranged in two parallel rows,
their active surfaces parallel to the cathode faces.   The arrange-
ment of electrodes, diaphragm, and cathode is such that the dia-
phragm lies against the cathode, while between the diaphragm
and active surfaces of the electrode is a space for electrolyte.
The leading-in portion of the electrodes extends through the
chlorine chamber and cell cover and is connected outside of
the cell to a copper bus with shunts of a type that reduce the
power losses to a minimum.   Brine is admitted to the anode
compartment through a special feeding device which maintains

the electrolyte in the cell at a constant level higher at all times than the liquid-tight joint between the anode and cathode compartments. The electrolyte from the anode compartment percolates through the permeable asbestos diaphragm and through the perforated cathode, and flows down the outside face of the cathode into the cell tank which forms part of the cathode compartment. When the cell is in operation, this electrolyte is decomposed into its major products of chlorine, caustic soda, and hydrogen, the chlorine being generated in the anode compartment and collected from the gas chamber. The caustic soda, with that portion of the cell electrolyte not decomposed, is collected in the cell tank and removed therefrom by gravity through a suitable seal to the salt caustic collection main. The hydrogen liberated in the cathode compartment is discharged into the atmosphere or utilized in some process.

Billiter Cell. According to reports of American technical teams who studied German plants after the Second World War, the Billiter cell plant at Bitterfeld consists of 352 cells rated at 10,000 amp, and 192 in the Wolfen rated at 5,000 amp. The feed brine is prepared in a manner similar to that used in the mercury cells, except that sulfates are permitted to remain and are as high as 6 g Na_2SO_4 per liter. The 10,000-amp Billiter cells operate at 4.5 volts per cell, 94 per cent current efficiency, and 1.67 kwhr per lb of chlorine. The effluent contains between 110 and 140 g of NaOH per liter and about 0.125 g of $NaClO_3$ per liter. The cathode current density was designed at 0.65 amp per sq in. The graphite consumption is 4.5 lb per 1,000 lb of chlorine on German graphite and 4.1 on Acheson. The anode gas is 98 per cent chlorine, 0.1 per cent H_2, and 1.0 per cent air.

The cells are of the horizontal, diaphragm type containing 107 sq ft of diaphragm. The external dimensions are about 10 by 18 ft and about 2 ft high. The body is of steel which is bare in the cathode (bottom) section and brick-lined above the cathode. Eight sandstone tops about 4½ by 4½ ft by 2½ in. carry the anode graphite leads, which are 4 by 18 in. and cut down to 2½ in. in diameter for the connections. One hundred twelve anodes, 2½ by 3 by 24 in., are employed. Apparently the anode current density was about 1.2 amp per sq in. The new anodes are slotted with four saw cuts to a depth of 1 to 1½ in. and are placed 0.4 in. above a new diaphragm surface.

The sandstone tops were luted with putty, and the graphite anode leads were sealed with a synthetic waxlike resin. Anode life was about 9 months, whereas a diaphragm's life was 6 months. The cell, therefore, is dismantled for diaphragm renewal at 6 months; 3 months later the anodes are renewed and the diaphragm is cleaned. The new anodes then run 3 months, the diaphragm is renewed, and the next assembly operates for 6 months.

The cathode chamber has rods on edge supporting the cathode about 4 in. above the bottom. The closely woven cathode screen rests on the rods and supports the diaphragm which was composed of four parts of long-fiber asbestos and 100 parts of finely ground $BaSO_4$. These are mixed intimately. Blue fiber asbestos from Canada or South Africa was preferred. Glass cloth has been tried but found to be soluble. Single and multiple asbestos papers have been tried but were considered too weak.

Brine level was indicated by a float. The inventory of brine in the cell was very large, and hand regulation was satisfactory. Hydrogen lines were insulated as they left the cells, and corrugated effluent devices were used to prevent leakage of current through the cell effluent.

Bridge cranes of about 1-ton capacity span all cells for handling the sandstone slabs, and the cell body was seldom moved and probably has a life of 10 years. Labor requirements were given as 20 men per day to operate and maintain 160 Billiter cells. This is equivalent to 1.6 man-hours per 1,000 lb of chlorine. The floor space for cells only is about 600 sq ft per 1,000 lb of chlorine per day.

The Billiter cells at Wacker at Burghausen are rated at 6,000 amp and are smaller than those described at Bitterfeld. The fundamental data, such as current density, graphite life, and operational life, are the same.

Operating data are shown in Table 63 and may be compared to American cells.

Buck-McRae Cell. The Buck-McRae was similar in construction to the Allen-Moore but in addition had a central diaphragm and cathode. The entire unit fitted in an iron tank and was enclosed at the top by a concrete block or blocks through which the graphite anodes rose. Figure 126 shows the structural features of the cell, including the iron containing tank, the
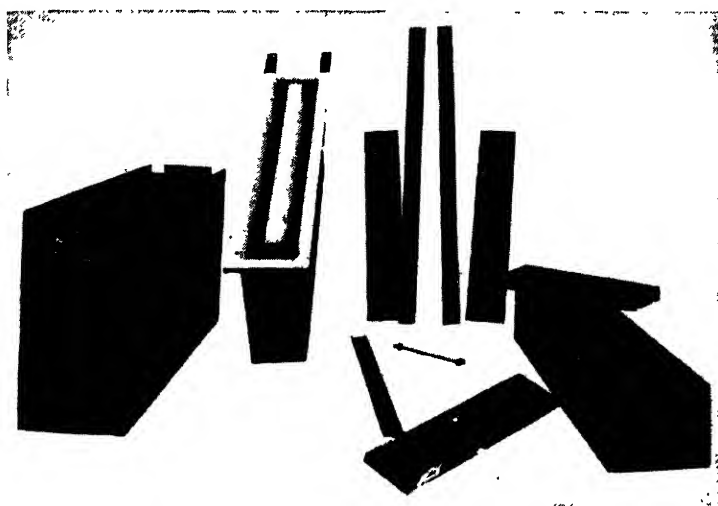
FIG. 126. Buck-McRae cell, before assembly. (*Jessup and Moore Paper Company.*)
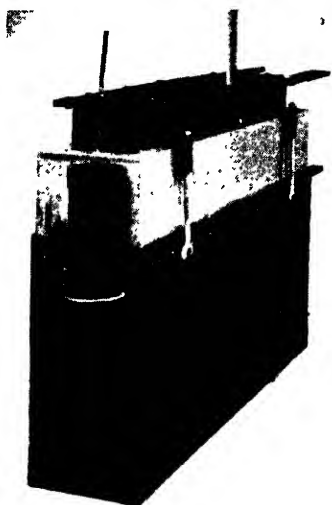
FIG. 127. Buck-McRae cell, completely assembled. (*Jessup and Moore Paper Company.*)
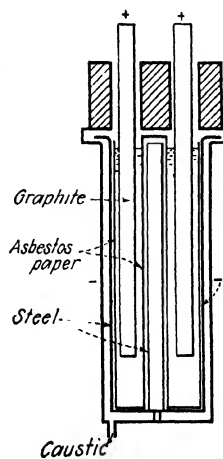
FIG. 128. Buck-McRae cell.

outer and inner diaphragms and cathodes made of expanded or perforated steel, graphite anodes which are flat slabs, and the cell cover. The assembled cell is shown in Fig. 127. The construction of the cell is illustrated in Fig. 128. Simplicity of construction is a feature. The unit found application in connection with pulp and paper manufacture but is no longer operated.

European Diaphragm Cell. This cell is of the vertical type with unsubmerged cathodes and contains, according to its capacity, one or several cathodic elements placed in cathode boxes. The cathodes are formed by perforated sheet boxes in the shape of a U or a W. Each cathode has a surface area equivalent to 1,000 amp, but they may be overloaded 25 per cent. Commercial cells may be built up to 7,500 amp, in which case three W-shaped cathodes, each of 2,500 amp capacity, are placed in the same tank. Figure 129 illustrates a W-type cathode of 2,000 to 2,500 amp. Brine feed to the cell is through a hydraulic
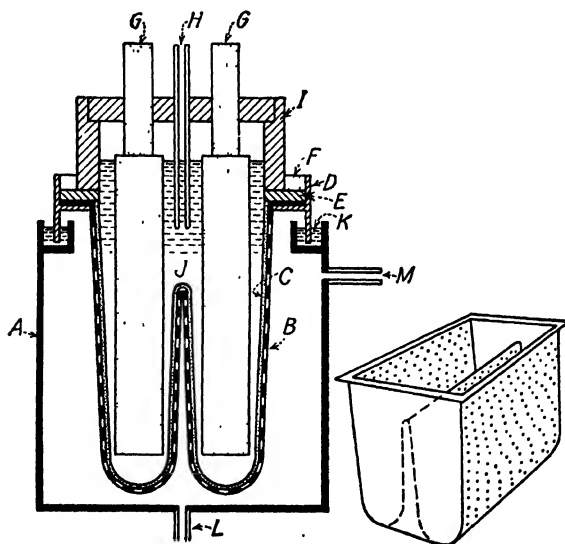
FIG. 129. Diagrammatic sketch of the double diaphragm cell. *A*, cathode tank; *B*, perforated cathode; *C*, diaphragm of asbestos paper and tissue; *D*, T-iron frame to which the perforated cathode is welded; *E*, special joint which, together with joint *F*, ensures tightness inside the cell; *G*, artificial graphite anodes; *H*, brine feed; *I*, anode box or chlorine trough, made of refractory material not affected by chlorine gas or by electrolyte *J*; *K*, hydraulic joint between cathode tank *A* and cathode *B-D*; *L*, caustic exit; *M*, hydrogen outlet.

level regulator. The feature of the cell is the ease of replacement of the diaphragms. These have an average service life of about 9 months. The cathode, fixed to the T-iron frame, is readily lifted up. The anodes, the anode box, and the cathodes are all taken out of the tank in one operation. Another assembly can then be inserted directly in the line with little loss of time. A typical European cell room of 2,500-amp cells is shown in Fig. 130.
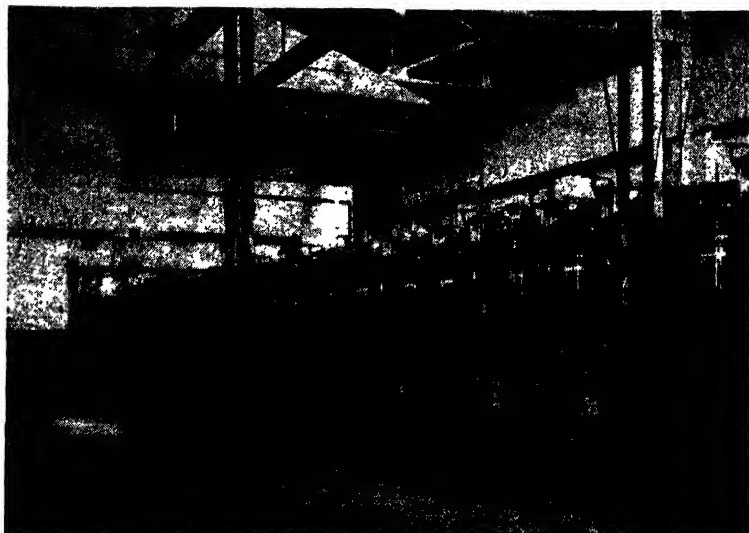
Fig. 130. Cell room showing 2,500-amp diaphragm-type cells.

Larchar Cell. This cell design, employed in a paper mill, is such that almost all the anode surfaces are adjacent to diaphragms and cathodes to give a higher ampere unit than Allen-Moore or Nelson designs. Figure 131 illustrates the construction, and operating data are given in Table 63.

Nelson Cell. The Nelson cell is rectangular in shape and consists of a steel tank into which is inserted a U-shaped perforated sheet-steel cathode plate carrying the asbestos diaphragm. The diaphragm chamber is closed at the ends by cement-mortar blocks. The tank is covered at the top by a slate gas dome on the top of which are slate slabs supporting the anodes. These are 4- by 4-in. square graphite blocks into which cylindrical graphite connectors are threaded and which in turn bolt to a copper busbar on the outside of the cell. The construction of

the cell can be seen from Fig. 132. Carefully purified brine is fed into the anode compartment by an automatic feed. Steam is introduced into the cathode chamber to maintain the diaphragms in an open condition. Operating data of commercial
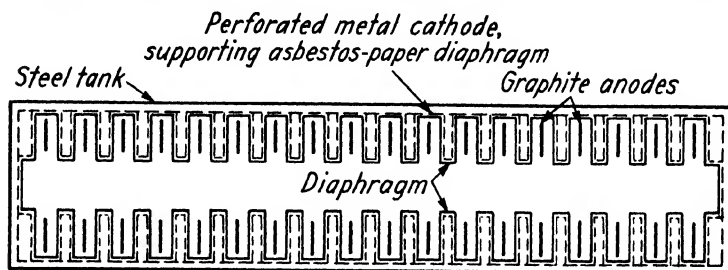
FIG. 131. Horizontal cross section of Larchar cell showing anode, cathode, and diaphragm arrangement.

cells are given in Table 63. The Nelson cell was used at the chlorine plant at Edgewood Arsenal which was the first plant of 100 tons Cl_2 per day capacity. There is no provision for circulating brine through the anode compartment, so that all cell
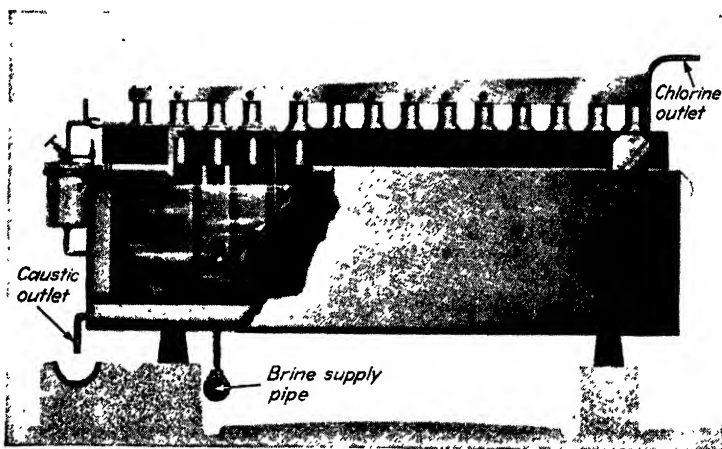
FIG. 132. Nelson cell, with portion of steel tank broken out to show the interior arrangement of the cell.

liquor eventually passes through the diaphragm to the cathode compartment.

Cylindrical Cells. The cells of a cylindrical shape are represented by the designs of Gibbs, Wheeler, and Vorce. It is

claimed that they are simpler, easier, and cheaper to construct, and allow stronger construction for a given weight of material than do the rectangular designs. The graphite rod anodes are arranged around the inside of a diaphragm. There are no ends to the anode chamber as in the rectangular cells. Higher output per unit of floor space is claimed. From this viewpoint, cylindrical units must be small. The floor space required will be proportional to the square of the output. •

Gibbs Cell. The early cylindrical cell is due to A. E. Gibbs of the Pennsylvania Salt Manufacturing Company. Figure 133
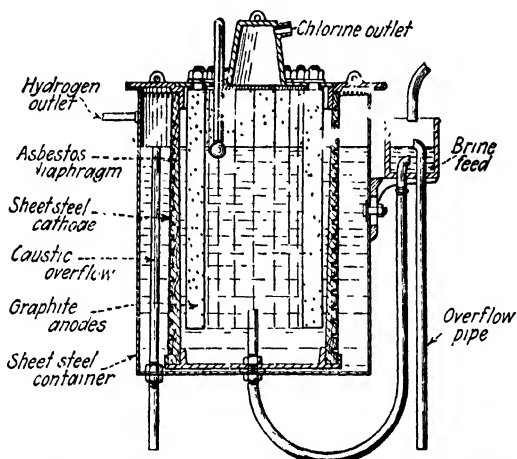
Fig. 133.   Original Gibbs cell (from U.S. Patent 874,064).

represents the original Gibbs cell.[11] It was first designed to work with a submerged cathode, and the cathode compartment was filled with alkali. The anodes are arranged in a circular ring around which are the diaphragm and the cathode. The entire cell was enclosed in a cylindrical sheet-steel tank. The diaphragm was of asbestos and increased in thickness from top to bottom to allow for the difference in hydrostatic pressure and to cause the rate of percolation to be the same at the top and bottom. The diaphragm and cathode sheet were attached above and below to cast-iron rings covered with chlorine-resistant hard rubber. The upper of these rings rested on the outer steel casing

[11] Gibbs, A. E., U.S. Patent 874,064 (Dec. 17, 1907).

and carried the chlorine dome or outlet as well as the anode compartment cover from which the anodes hung.

In its commercial application, the Gibbs cell now uses an unsubmerged cathode with concrete replacing the rubber-covered cast-iron parts. Except for minor details, it is similar in most respects to the Vorce cell. Figure 134 shows a Gibbs cell plant. Commercial operating data on the Gibbs cell are given in Table 63.

F. G. Wheeler and L. D. Vorce were associated with Gibbs

Fig. 134. A Gibbs cell plant. (*Canadian Industries, Ltd.*)

during the development period of the Gibbs cell, and both later patented cells which bear their names.

Vorce Cell. The Vorce cell is of the cylindrical diaphragm type operating with unsubmerged cathode. The cathode is of steel wire mesh or perforated metal to which are attached lugs and angles for clamping the vertical seam. The cathode is housed in the steel drum or cylinder, at the bottom of which is a threaded opening for withdrawing the caustic effluent with a drip cup attached so that the outgoing caustic liquor may be broken up into drops to avoid current loss. Within the cathode is placed the anode which consists of twenty-four 2- by 2- by 36-in. graphite sticks. The end of each stick is machined to pass through an opening in the concrete cover or ring and secured firmly in position by a lock nut. Proper gaskets are applied, when making up this joint, to prevent leakage. Thus there is no

joint in the carbon sticks within the cell with its attendant corrosion and resistance. Current is supplied to each carbon by means of an annular copper strip punched for bolting to the carbons. The method of connecting from cell to cell by flexible cables, called "crowfeet," permits the assembling of the cells without loss of time required for close alignment which is necessary when rigid bar connection from cell to cell is practiced.
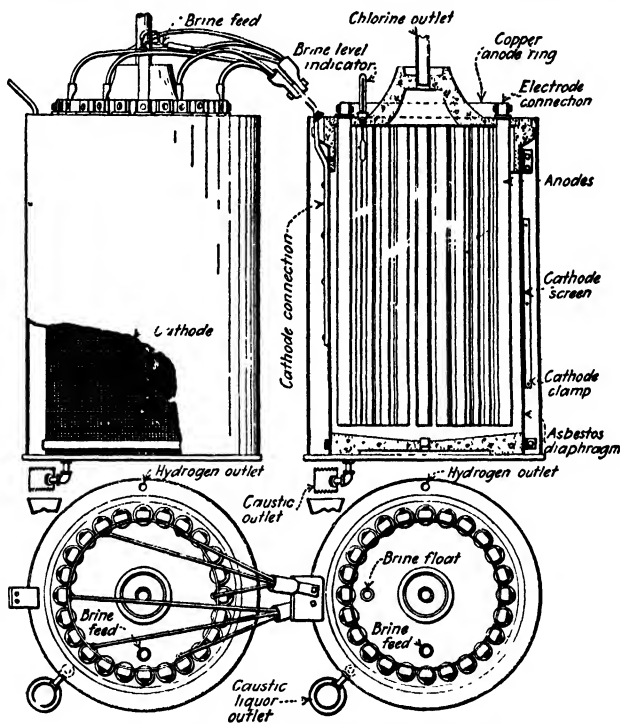
Fig. 135. Construction of the Vorce cell.

Construction details of the Vorce cell are given in Fig. 135. The base of the cell carries a concrete plate or pedestal which holds the cathode in place. At the top the cathode is attached to a concrete ring which rests on the external cylinder and which, in turn, carries a concrete cover from which the anodes depend. This cover is so shaped that it forms the chlorine bell through which the chlorine outlet passes. Figure 136 shows a commercial Vorce cell installation. A 1,000-amp Vorce cell weighs less than 600 lb. Its features are small floor space, efficient and
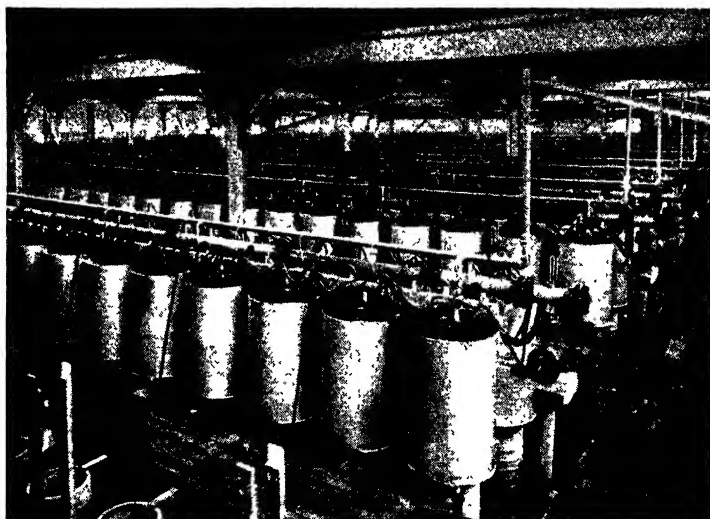
Fig. 136.   A Vorce cell room.   (*Westvaco Chlorine Products, Inc.*)

inexpensive anodes, simplicity, accessibility, and strong cheap construction.   Operating data on Vorce cells are given in Table 63.

In the operation of cylindrical cells it is as important as in connection with rectangular units that the brine be freed from all lime, magnesia, and iron, and that the sulfates be prevented from concentrating to a point where they are subject to electrolysis.   Sulfuric acid and sulfate electrolysis products cause anode disintegration and losses.   Failure to use pure brine results in clogging the diaphragm, increases the concentration of the caustic, and depletes the salt in the anode compartment to a point where the current can decompose the water.   The oxygen thus formed unites with the carbon with consequent increase of H_2CO_3 in the chlorine gas and the ultimate destruction of the anodes.   All these militate against high efficiency.

In the Gibbs and Vorce cells it is possible to circulate the brine to the anode compartment and maintain it in a saturated condition by running it over fresh salt.   Such practice is often followed, with gain in current efficiency.   The matter of current capacity of the cells is largely a question of economics.   The cells will run successfully at moderate voltages with currents of 1,000 amp.   Increased current above that point raises the voltage slightly, thus lowering power efficiency.   Operating below

TABLE 63. ELECTROLYTIC CHLORINE AND CAUSTIC DIAPHRAGM CELLS

	Griesheim	Le Sueur	Larchar	Billiter
Cell shape	Rectangular	Rectangular	Rectangular	Rectangular
Voltage across cell	3 65–3 85	4 0	3 2–4 0	4 5
Current per cell, amp	2,500	2,400	3,600	10,000
C.d., anode, amp/sq in.	0 13	0 17	0 30	1 25
C.d., cathode, amp/sq in.........		0 26	0 22	0 65
Current efficiency of cell, %	80	85	92 0	94
Energy efficiency of cell, %. . .	48–50	49	56 0	
Lb NaOH per kwhr	0 68	0 70	0 75	
Lb Cl₂ per kwhr .	0 62	0 62	0 666	
Kwhr/lb Cl₂				1 67
Anode material	Carbon or magnetite	Graphite	Graphite	Graphite
Cathode material	Iron	Iron -wire netting	Perfor'ed iron	Woven screen
Diaphragm:				
Material	Portland cement	Asbestos paper	Asbestos	Asbestos and BaSO₄
Arrangement	Vertical	Horizontal	2 or 3 thicknesses	Vertical
Type	Submerged	Submerged	Paper	
Cell proper material	Iron coated with thermal insulator	Iron, cement-lined	Steel or wrought iron	Steel
Anode life, days.	Carbon 360. magnetite 700	5 years, av.	250	270
Anode consumption, lb/ ton Cl₂	.. ..			9
Average operating period of cell, days	....	180	250	
Raw material	NaCl	Brine, feed 98% sat'd, brine in cells 77% sat'd.	Saturated NaCl brine	
Concentration of cathode alkali	40–60 g/l	110–125 g/l	108 g/l	(Effluent) 110–140 g/l caustic, 0 125 g/l NaClO₃
Salt concentration, cathode alkali	150–175 g/l	.. ..	150 g/l	
Size of anode	.	80 anodes, 3″ × 4″ × 23″	37″ × 5″ × ¾″	112 anodes, 2½′ × 3″ × 24″
Size of cathode	....	Active surface, 63 sq in.	14,100 sq in.	
External measurements of cell	15′8″ × 10′10″ × 3′4″	16.6′ × 5′ × 1.7′	72″ × 24″ × 33½″ deep	18′ long, 10′ wide 2′ high

1,000 amp results in a lower voltage with higher power efficiency. This is a point for each plant to determine by balancing power cost against added investment. The comparatively low cost of the cell permits the operation at a current substantially below 1,000 amp where power charges are high. Double cathode cells of higher capacities have been developed.

TABLE 63. ELECTROLYTIC CHLORINE AND CAUSTIC DIAPHRAGM CELLS—
(*Continued*)

	Townsend	Giordani-Pomilio	Hooker type "S"	Hooker type "S-3"
Cell shape.	Rectangular	Rectangular	Square	Square
Voltage across cell	4 55	3 3-3 8	3 20-3 75	3 75
Current per cell, amp	5,000	3,000-3,200 normal	5,000-10,000	20,000
C.d., anode, amp/sq in.	1 23	0 45 0 52	0 32-0 64	0 64
C.d., cathode, amp/sq in	0 645	0 32-0 39	0 27-0 54	0 54
Current efficiency of cell, %	96	93-96	94-96	96
Energy efficiency of cell, %	48 5	58-64	68-58 5	58 5
Lb NaOH per kwhr .	0 695	0 80	0 96-0 83	0 83
Lb Cl₂ per kwhr	0 617	0 70	0 86-0 74	0 74
Kwhr/lb Cl₂			1 16-1 35	1 35
Anode material	Graphite	Graphite	Graphite	Graphite
Cathode material	Steel and wire screen	Perforated iron sheet	Steel and wire screen	Steel and wire screen
Diaphragm:				
Material	Asbestos paper	Asbestos fibers to form sheet on diaphragm	Deposited asbestos	Deposited asbestos
Arrangement	Vertical	Vertical	Vertical	Vertical
Type	Submerged	Submerged on the anodic side	Submerged	Submerged
Cell proper material	Concrete and steel	Cement	Concrete and steel	Concrete and steel
Anode life, days	350	300-500	500-360	360
Anode consumption, lb/ton Cl₂				7
Average operating period of cell, days	Diaphragm run 40 days	200-300	Diaphragms run 100-200 days	Diaphragms run 100-200 days
Raw material	Brine	Saturated purified brine	Brine	Brine
Concentration of cathode alkali	136 g/l	120-180 g/l	135-138 g/l	135-138 g/l
Salt concentration, cathode alkali	14-16%	110-150 g/l	14-15%	14-15%
Size of anode	18 anodes, 1¼" × 12½" × 18"	1,300 × 200 × 75 mm (approx. 51" × 8" × 3")	90 anodes, 1¼" × 6¼" × 18"	128 anodes, 1¼" × 6¼" × 24"
Size of cathode	Active surface 54 sq in.	1,000 × 3,300 mm (approx. 39" × 129")	Active surface 129 sq ft	Active surface 258 sq ft
External measurements of cell	1'8¼" × 16'2" × 5'4" high, pedestal 1'9½" add'l	360 × 150 × 19 cm, (approx. 11.7' × 4.87' × 0.6')	4'5⅜" × 4'11½" × 3'7⅝" high, pedestal and insulator 10½" add'l	4'8¾" × 5'3¼" × 4'6" high, pedestal and insulator 10½" add'l

TABLE 63. ELECTROLYTIC CHLORINE AND CAUSTIC DIAPHRAGM CELLS—
(*Continued*)

	Hargreaves-Bird	Allen-Moore	Nelson	Gibbs
Cell shape	Rectangular	Rectangular	Rectangular	Cylindrical
Voltage across cell	4 2	3 3–3 80	3.75 av.	3 43
Current per cell, amp	3,000	1,500–1,200	1,000	800
C.d., anode, amp/sq in	0 03	0 406–0 22	0 30	0 12¹
C.d., cathode, amp/sq in	0 21	0 24–0 31	0 34	0 31¹
Current efficiency of cell, %	90	90–95	93–95	92–95
Energy efficiency of cell, % … .	50	63 58	56 60	62
Lb NaOH per kwhr	0.914 Na₂CO₃	0 905–0 750	0 76	0 83
Lb Cl₂ per kwhr	0 62	0 8–0 665	0 67	0 74
Kwhr/lb Cl₂	1 61	1.25–1.5	1 5	1.35
Anode material	Graphite	Graphite	Graphite	Graphite
Cathode material	Perforated steel	Perforated steel	Perforated steel sheet and woven steel wire	Steel
Diaphragm: Material	Composition	Asbestos paper	Asbestos paper and cloth	Asbestos paper
Arrangement	Vertical	Vertical	Vertical	Vertical
Type.	Free	Free	Free	Free
Cell proper material	Cast-iron casing, acidproof brick lining	Steel and concrete	Steel tank, asbestos board and slate gas dome	Steel and cement composition
Anode life, days	750	425–900	900	600
Anode, consumption, lb/ton Cl₂				
Average operating period of cell, days	360	360	180–360	120
Raw material	Saturated brine	Salt brine, 300 g/l cell intake	NaCl	Saturated brine
Concentration of cathode alkali	170 g/l Na₂CO₃	About 90–110 g/l caustic	100 g/l	120 g/l
Salt concentration, cathode alkali		About 200–170 g/l	15 2%	140–170 g/l
Size of anode	72 anode plates, 16½″ × 9″ × 2″	Active surface 3,696 sq in.	14 anodes, 4″ × 4″ 17″	2″ × 2″ × 36″
Size of cathode.	10′ × 5′	6181.50 sq in.	77½″ × 43½″ U-shaped	36″ × 72″
External measurements of cell	11′6″ × 7′ × 1′6″	8′6″ × 1′2½″ × 3′, pier and insulator 1′5″	6′6½″ × 11½″ × 2′10″	26″ diam. × 36″

TABLE 63. ELECTROLYTIC CHLORINE AND CAUSTIC DIAPHRAGM CELLS— (*Continued*)

	Vorce	Vorce double cathode	Wheeler	Tucker-Windecker
Cell shape	Cylindrical	Cylindrical	Cylindrical	Cylindrical
Voltage across cell	3 5–3 8	3 7	3.6	3 5
Current per cell, amp	950–1,000	1,000–2,750	1,200–1,600	1,400
C.d., anode, amp/sq in.	0 14[1], 0 34[2]	0.34 at 1,600 amp	0 14[1]	0 625
C.d., cathode, amp/sq in	0.35[1], 0.5[2]	0.43 at 1,600 amp	0 37[1]	0 611
Current efficiency of cell, %	94–96	94–97	96–99	94
Energy efficiency of cell, %...	61–62	65 5–68	60–62	62
Lb NaOH per kwhr	0 86	0 93	0 83	0 88
Lb Cl_2 per kwhr	0.79	0 86	0 74	0 78
Kwhr/lb Cl_2	1.27	1 16	1 35	1.28
Anode material	Graphite	Graphite	Graphite	Graphite sticks
Cathode material	Perforated steel	Perforated steel	Special weave wire cloth	Perforated sheet steel
Diaphragm:				
Material	Asbestos paper	Asbestos paper	Asbestos paper	Asbestos paper
Arrangement	Vertical	Vertical	Vertical	0.025″ thick paper on cathode; 0.050″ thick paper on 0.025″
Type	Free	Free	Free	Wrapped
Cell proper material	Steel and cement composition	Steel and cement composition	Quartz-asbestos-cement, asphalt treated	Steel
Anode life, days	450	450	480–600	360–400
Anode consumption, lb/ ton Cl_2				
Average operating period of cell, days	120–180	180–270	150–200 days per diaphragm	
Raw material	Saturated brine	Saturated brine	Hot brine, 300 g/l	NaCl brine
Concentration of cathode alkali	90–105 g/l	106 g/l	110–120 g/l	110–115 g/l NaOH
Salt concentration, cathode alkali	16%	15.79%	140–170 g/l	145–150 g/l
Size of anode	24 anodes, 2″ × 2″ × 36″	24 anodes, 2″ × 2″ × 36″	28 anodes, 2″ × 2″ × 32″	28 per cell, 2″ × 2″ × 42″
Size of cathode	22″ diam. × 34″	22″ + 16″ = 36″ × 36″	34″ × 80″	23″ diam. × 42″ high
External measurements of cell	26″ diam. × 42″	26″ diam. × 42″	29″ × 36″	26¼″ diam. × 45″ high

[1] Calculated from entire anode or cathode surface.

[2] Calculated from active anode or cathode surface.

Wheeler Cell. The Wheeler cell differs in one essential feature of construction from the Gibbs and Vorce units. The cell cover and the weight of the anodes are supported by a central cylindrical pedestal made of concrete. A number of apertures in the pedestal allow the entrance of fresh brine which enters at the base of the cell. The cover, base, and pedestal are made of concrete consisting principally of quartz sand, asbestos fiber, and cement, the formed article being later impregnated with Trinidad asphalt. The diaphragm is of asbestos paper, the cathode of woven steel wire screen of special design. Graphite anode lives are stated to be as much as 2 years, and anode consumption of the order of 10 lb per ton of caustic. The outer jacket of the cell is of sheet steel and rests in flanges on the concrete base. As in the Gibbs and Vorce cells, there is an adjustable feed cup for brine regulation. Operating data are given in Table 63. Figure 137 shows the construction of the Wheeler cell.
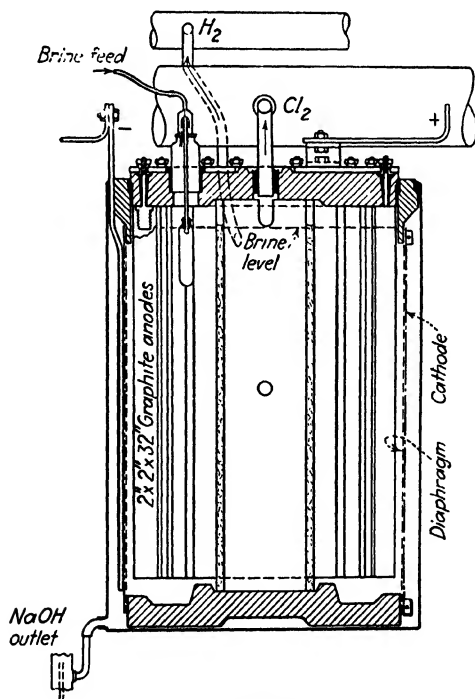
Fig. 137.   Wheeler cell.

TABLE 64. OPERATING DETAILS FOR MERCURY CELL PREPARATION OF KOH

	Raw material	Brine
KCl	90%	345–350 g/l
NaCl...	5 7%	
MgCl$_2$	0 05%	
CaCl$_2$	0 003%	
Insolubles	Balance	
K$_2$CO$_3$	. . . . .	0.5–0.6 g/l
KOH	. .	0.1–0.15 g/l
K$_2$SO$_4$..	.. .. .	3–4 g/l
KClO$_3$..	.. ..	2–3 g/l
CaO	. . .	0.4–0.5 g/l
NaCl....	. . . . . .	0.8 g/l
Cell:		
Length......	7 m	
Form	800-mm I beam	
Slope..	15 mm in 7 m	
Number of anodes. . . .	37	
Decomposer, width.......	250 mm	
Decomposer, graphite . . .	Slotted blocks, 165 mm long × 165 mm wide × 55 mm thick	
Brine flow...........	440–450 l/hr	
Brine flow feed	345–350 g/l	
Brine flow exit	270–280 g/l	
Voltage per cell.. .. .	4.1–4.3 (4.5 for NaOH)	
Amperes per cell	12,000	
Cathode c.d.	2,000 amp/sq m	
Current efficiency .. .	92–94 (94–96 for NaOH)	
Anode life ..	7–8 months (60,000 kilo-amp-hr)	
Temperature brine feed.	50–60°C	
Temperature brine exit.. .	75–80°C	
Temperature decomposer liquor .	80–90°C	
Decomposer cleaning cycle......	2–4 months	
Spacing, graphite and amalgam, mm.................. .	7 (5 for NaOH)	
Thickness of mercury..... .	5 mm	
Mercury per cell.......... . .	750–800 kg	
Hydrogen content of Cl$_2$ gas...	1.5–2%	
Per cent K in amalgam........	0.20	
Product:		
Total alkalinity (KOH). ..	50–50 5%	
KOH.................	49.7–50 4%	
K$_2$CO$_3$............... ..	0.1–0.4%	
NaOH.	0.2–0.4%	
KCl.....................	0.01–0.02%	
K$_2$SO$_4$....................	· 0.001–0.01%	
KClO$_3$...............	0.001–0.005%	
Fe$_2$O$_3$....................	0.002–0.05%	

Tucker-Windecker Cell. This unit is cylindrical but designed for higher current density at anode and cathode. Operating data are given in Table 63.

Electrolysis of Potassium Halides. KOH may be produced by the electrolysis of KCl either in diaphragm or in mercury-type cells. The production is small in comparison to NaOH. Operational details in large size mercury cells in Germany are given in Table 64.

Liquid Chlorine. The transportation of liquefied chlorine has assumed large proportions.[12] It is shipped in seamless steel cylinders ranging in size from 10- to 150-lb capacity, the smaller cylinders being employed for experimental purposes; or in multiple-unit tank cars, the units being steel containers of 1-ton capacity; or large single-unit tank cars of hammer-welded construction, made of steel and having a capacity of 15 tons of liquid chlorine at 21°C. The transportation of chlorine, the construction of containers, specifications for these, inspection, and testing are regulated by the Interstate Commerce Commission under Group D: Compressed Gases. Chlorine is in the dangerous articles index of the I.C.C.

Liquid chlorine in containers is in equilibrium with its own vapor pressure at the temperature of its surroundings. It is generally withdrawn from containers in the form of gas, although, if the containers be held in an inverted position, as is the case of cylinders, liquid chlorine may be obtained. Figure 138 gives the vapor-pressure curve of chlorine at various temperatures. If the rate of feed from a container be so rapid that evaporation within the container cools the liquid content materially, the pressure will drop, and heat will have to be applied externally to maintain temperature and pressure.

HYPOCHLORITES

It has been previously pointed out that, if the products of salt electrolysis be mixed, hypochlorites will result from the reaction

$$Cl_2 + 2NaOH \rightleftarrows NaCl + NaClO + H_2O$$

or from the slower reaction

$$Cl_2 + H_2O \rightleftarrows HClO + HCl$$

[12] WELLS, H. P., MABEY, H. M., and ROWLAND, J. M., *Trans. Am. Electrochem. Soc.*, **49**, 43 (1926).

where self-oxidation and reduction of the chlorine take place, in that molecular chlorine (with an assumed zero valence) is reduced to chloride ion (in which the chlorine valence is -1) and oxidized to hypochlorite (in which the chlorine valence is $+1$). It follows that hypochlorite produced from chlorides
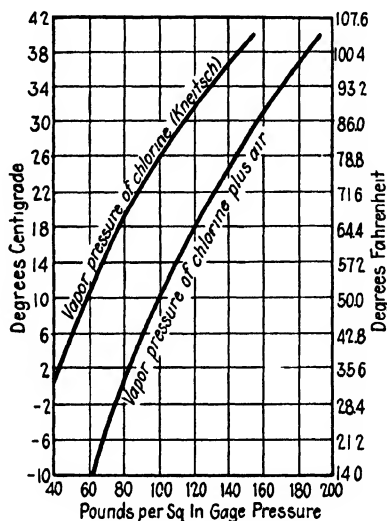
FIG. 138.   Chlorine vapor-pressure curve at varying temperatures.

involves a valence change of 2 and, per equivalent, requires $2F$. The summary reaction is therefore:

$$2NaCl + 2HOH \rightleftarrows 2NaOH + Cl_2 + H_2$$
$$Cl_2 + 2NaOH \rightleftarrows NaCl + NaClO + H_2O$$
$$\overline{NaCl + HOH \rightleftarrows NaClO + H_2}$$
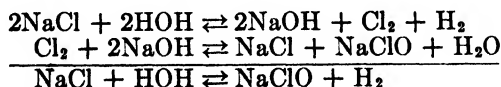
which is almost quantitative if temperatures be kept low so that maximum chlorine concentration be obtained. The effect of temperature on the solubility of chlorine in brine and water is given in Fig. 139.[13]

Under equilibrium conditions, HClO concentration will be high at the anode and formation of chlorate by chemical reaction is possible,

$$2HClO + HClO \rightarrow HClO_3 + 2HCl$$
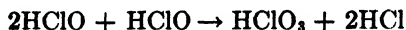
[13] HOOKER, A. H., *Chem. & Met. Eng.*, **23**, 964 (1920).

while at the cathode, as a result of mixing and migration, HClO concentration will be low. Some losses may occur by cathodic reduction or by freshly liberated (nascent) hydrogen:

$$HClO + H_2 \rightarrow HCl + H_2O$$
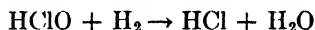
Conditions of hypochlorite concentration may be reached where the oxidation at the anode may be balanced by the reduction at the cathode; zero yield will then result. The addition of
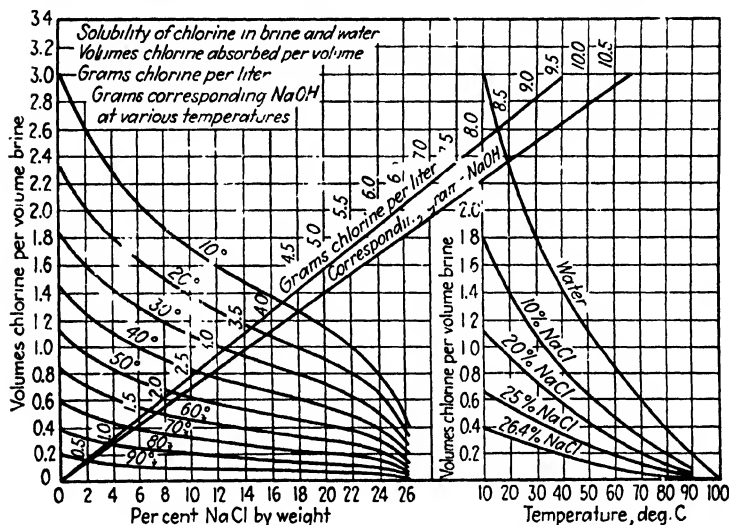
FIG. 139. Solubility of chlorine in brine and water.

soluble chromates or sulfonated oils to the electrolyte forms thin cathode diaphragms of insoluble chromates which markedly decrease cathodic reduction. These diaphragms are broken down by acidic or alkaline conditions, so that almost neutral electrolytes are preferred.

The electrolysis of a brine solution follows a course such as that given by Foerster[14] in Fig. 140. At equilibrium, chlorine production consumes two-thirds of the current, the chlorine reacting with NaOH to give hypochlorite, while ClO⁻ ion discharge consumes the remainder. ClO⁻ ion discharge gives free oxygen, while chlorate oxygen results ultimately from the chlorine-

[14] FOERSTER, F., "Elektrochemie wässeriger Lösungen," p. 672, J. A. Barth, Leipzig, 1923.

caustic reaction[15] summarized as

$$6ClO^- + 3H_2O \rightarrow 6H^+ + 2ClO_3^- + 4Cl^- + 1\tfrac{1}{2}O_2 + 6e$$

and

$$H^+ + OH^- \rightarrow H_2O$$

and

$$Cl^- + Cl^- \rightarrow Cl_2 + 2e$$
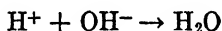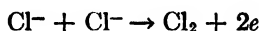
An analysis of the curves shows that hypochlorite formation rises rapidly and becomes constant and that chlorate formation
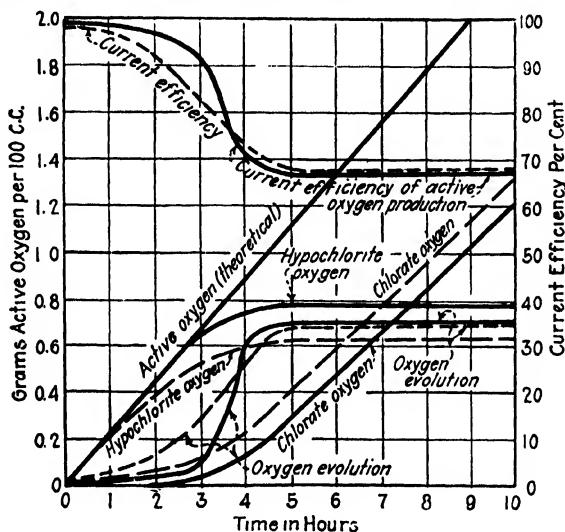
FIG. 140. The course of a typical electrolysis of a neutral brine solution. Electrolyte, saturated NaCl + 0.2 per cent K_2CrO_4; temperature, 12°C; anode current density, 0.43 amp per sq in. (0.067 amp per cm²); solid lines platinized platinum anodes, dotted lines smooth platinum.

becomes important when hypochlorite formation rate slows down. The chlorate formation continues so that, at 66.7 per cent current efficiency, hypochlorite concentration is constant but $NaClO_3$ is still increasing. Oxygen production at the anode and hydrogen at the cathode consume the remaining portions of the current. The industrial production of hypochlorite solutions employs electrode arrangements allowing undisturbed diffusion layers at the anode, neutral electrolytes, low temperature, high anodic current density, the use of additions which form cathode films,

[15] FOERSTER, F., and MÜLLER, E., *Z. Elektrochem.*, **8**, 665 (1902).

concentrated NaCl solutions, and, if possible, platinized platinum electrodes.

In commercial cells carbon or graphite·electrodes are employed for large-scale units. In general, the electrodes are bipolar, being connected in series, the electrolyte circulating from one end of the containing tank to the other between the electrodes.[16] In the United States hypochlorite solutions are ordinarily made by dissolving chlorine gas in caustic solutions. In this country electrolytic hypochlorite cells are available only in small sizes for small uses of the product. In Germany much greater development has taken place of large-scale hypochlorite cells.

FLUORINE ·

In 1813 Davy was unsuccessful in electrolyzing HF. Moissan in 1885 found that KF could be dissolved in nonconducting anhydrous HF to produce a conducting solution. This he later electrolyzed at −23°C in a platinum U tube with Pt-Ir electrodes and isolated fluorine. In 1900 Poulenc and Meslous devised a fluorine cell of the diaphragm type. Copper was used for the cell container and the diaphragm as a fluoride film formed on the metal and insulated it. Military requirement for fluorine in connection with the Second World War brought the element into commercial tonnage production, the raw material being anhydrous hydrogen fluoride (AHF).

Cady, Rogers, and Carlson[17] in 1942 reviewed the prior art. The commercial cells depended upon (1) the choice of electrolyte, which in turn determined the materials of construction, and (2) the mechanical design of the cell. The electrolytes were all combinations of AHF and KF while experimental work had led to materials of construction as given in Table 65.

Schumb, Young, and Radimer[18] described the electrolytic preparation of fluorine from a fused bath of KF·2HF with carbon anodes, emphasizing control of the HF content to avoid polarization or "anode effect" troubles. LiF is introduced to

[16] ENGELHARDT, V., "Hypochlorite und elektrische Bleiche," p. 160, Technischkonstruktiver Teil.

[17] CADY, G. H., ROGERS, D. A., and CARLSON, C. A., *Ind. Eng. Chem.*, **34**, 443–448 (1942).

[18] SCHUMB, W. C., YOUNG, R. C., and RADIMER, K. J., *Ind. Eng. Chem.*, **39**, 244–248 (1947).

TABLE 65. MATERIALS OF CONSTRUCTION

Temp., °C	Composition	Cell body	Diaphragm	Cathode	Anode
−50 to −30	KF·12HF	Platinum	Platinum	Platinum	Platinum-iridium
50–60	KF·3HF	Copper, nickel	Copper, nickel	Copper, nickel	Nickel
100	KF·2HF	Iron	Iron	Iron	Nickel, graphite
250	KF·HF	Copper, magnesium	Copper, magnesium	Copper, magnesium	Graphite

control polarization. Murray, Osborne, and Kircher[19] described experimental Hooker 2,000-amp cells.

With the exception of one or two commercially impractical electrolytes, those recorded and known to be available were all different combinations of anhydrous hydrofluoric acid and potassium fluoride, anhydrous hydrofluoric acid itself being a nonconductor. There are four practical ranges of hydrofluoric acid concentration to choose from, each with its own operating temperature. A good deal was known or suggested concerning the possible materials of construction which could be used with each. Table 65 gives the available information.

The current-voltage relations are given in Fig. 141. Carbon anodes, steel cathodes with steel wire mesh for diaphragms in steel tanks with jackets, and KF·2HF electrolytes were used. Operating details for Hooker cells are given in Table 66. Pinkston[20] described the operation of a Harshaw 1,000-amp cell diagrammatically shown in Fig. 142. Operating data are given in Table 66. Additions of 1.0 to 1.5 per cent LiF were desirable to the KF·2HF electrolyte.

Downing and coworkers[21] described a cell for the electrolytic manufacture of fluorine, using carbon anodes in an electrolyte containing potassium fluoride and hydrogen fluoride in a mole

[19] MURRAY, R. L., OSBORNE, S. G., and KIRCHER, M. S., *Ind. Eng. Chem.*, **39**, 249–254 (1947).

[20] PINKSTON, J. T., JR., *Ind. Eng. Chem.*, **39**, 255–258 (1947).

[21] DOWNING, R. C., BENNING, A. F., DOWNING, F. B., McHARNESS, R. C., RICHARDS, M. K., and TOMKOWIT, T. W., *Ind. Eng. Chem.*, **39**, 259–262 (1947).

TABLE 66. OPERATING DETAILS OF FLUORINE PRODUCTION

	Hooker	Harshaw	du Pont	High temperature	Falkenhagen	Leverkusen
Cell, shape	Rectangular	Rectangular	Rectangular	Rectangular	Rectangular	Rectangular
Body	Steel	Steel	Steel	Monel	Elektron metal	Elektron metal
Jacket	Steel	Steel	Steel		Steel	
Length, width, height	. .	71¼" × 18½" × 24"		.4′ × 16″ × 4′	1,790 mm long × 680 mm wide × 900 mm high inside dimensions; 1,770 mm long × 1,310 mm wide × 1,485 mm high outside dimensions	3.14 m long, 480 mm wide, outside; 310 mm wide, inside; 480 mm high, 30 mm wall thickness
Voltage across cell	8 7	9 0-9 5	8 5-11	6-8	6-6 5	11
Current per cell, amp	2,000	1,000	1,500	600-650	2,00C	2,000
C. d., anode, amp/sq ft	71	100-200	75	300-325	60-72 (0.065-0.08 amp/cm²)	90 (0.1 amp/cm²)
Current efficiency of cell, %	65-70	95	90+	90-55	95	75-85
Energy efficiency of cell, %			20-30			72-85
Temp. of operation, °C	95-105	105-113	100	280-310	240-250	
Raw material	HF	HF	HF	HF gas	HF	HF
Electrolyte	KF·2HF	KF·2HF + 1-1.5% LiF	KF 2HF + LiF	KHF₂	KHF₂	KF·2.5HF
Weight, kg	. . . . .	. . . . .	. .	. . . . .	. . . . .	600
Anodes: Material	Carbon	Petroleum coke carbon	Carbon	Graphite	Graphite	Carbon
Length, width, thickness	18″ × 6¼″ × 1¼″	12″ × 1¼″ diam			46 mm thick × 460 mm wide (anode surface 30,000 cm²)	125 mm wide × 350 mm high × 50 mm thick
Number	28	15 sq ft			6	15
Life	2½-3 months		1,000 hr	500 hr	1 year	2½ years

TABLE 66. OPERATING DETAILS OF FLUORINE PRODUCTION.—(Continued)

	Hooker	Harshaw	du Pont	High temperature	Falkenhagen	Leverkusen
Cathodes:						
Material	Steel	Steel	Steel	Monel	Silver	Elektron metal
Length, width, thickness	....	.....	.....	34″ × 18″ × 4″	20 mm thick, 446 mm wide × 550 mm high (cathode surface 30 mm)	2.31 m long × 300 mm high × 7 mm thick
Number	....	....	.....	.	7	16
Anode-cathode distance	....	1½″	.....		30 mm	60 mm
Diaphragm:						
Material	Steel	Monel	Steel	Monel	Cast elektron metal	
Arrangement	Vertical screen	...	....	.	Chamber 4 mm wide slots 5·0 mm wide × 5 mm thick × 450 mm high	
Size	...	.	....			
Operating period of cell	.	..	1.000 hr			
Analysis of cell products.						
F %	..	..	Balance		98	
HF %	.	..	5–15			
N₂ %		...	1			
O₂ %		...	1			
Kwhr/lb.		2 8–3 0				
Kwhr/kwhr		0 3–0 35				

Fig. 141. Current-voltage relation of 2,000-amp fluorine cell.
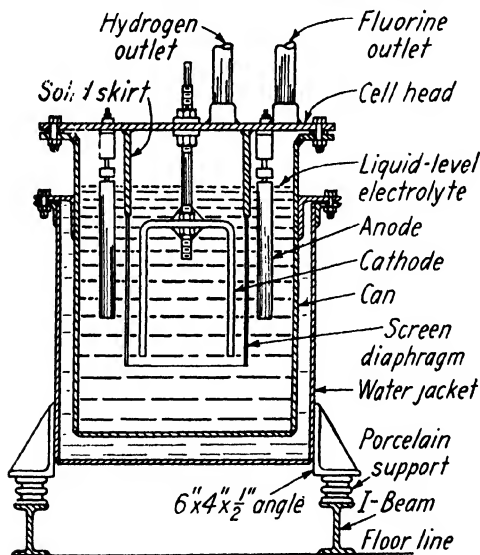
Fig. 142. Typical section of cell assembly.

ratio of 1:2. In large-scale operation the cells are placed in separate compartments in groups of three, all emptying into a common header and connected electrically in series. Some of the units have been operated for more than 5,000,000 amp-hr, producing in that time nearly 7,000 lb of fluorine with evidence

that longer lives can be expected. The unit is shown diagrammatically in Fig. 143. Operating details are shown in Table 66 as the duPont cell. The effect of anode material and cell life on voltage is shown in Fig. 144. Gall and Miller[22] described
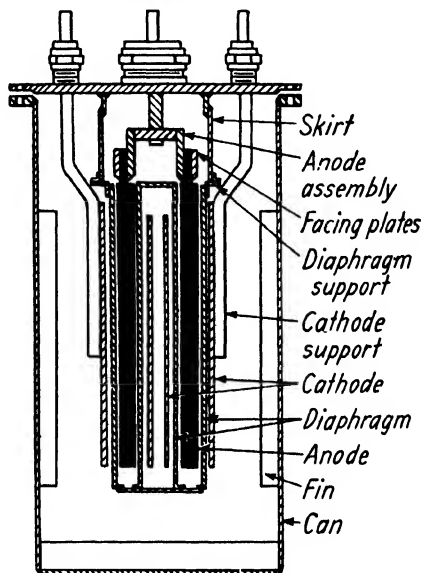
FIG. 143. Carbon anode fluorine generator.
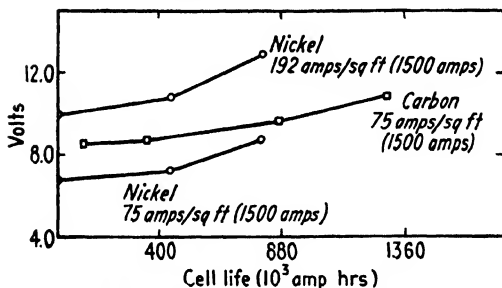
FIG. 144. Effect of anode material and cell life on voltage.

small-scale production of fluorine in a cell shown in Fig. 145. Fowler and coworkers[23] described the design and operation of a

[22] GALL, J. F., and MILLER, H. C., *Ind. Eng. Chem.*, **39**, 262–266 (1947).
[23] FOWLER, R. D., BURFORD, III, W. B., ANDERSON, H. C., HAMILTON, J. M., JR., and WEBER, C. E., *Ind. Eng. Chem.*, **39**, 266–272 (1947).

600- to 800-amp high-temperature fluorine cell. The cell contains about 100 lb of KHF_2 as electrolyte and is constructed of monel, steel and copper. The total weight of the cell is about 400 lb, and it occupies about 2 by 4 ft of floor space. The electrolyte temperature is kept constant by jacketing the cell with a bath. The bath is provided with a water-cooled reflux condenser. The life of the cell without repair is determined
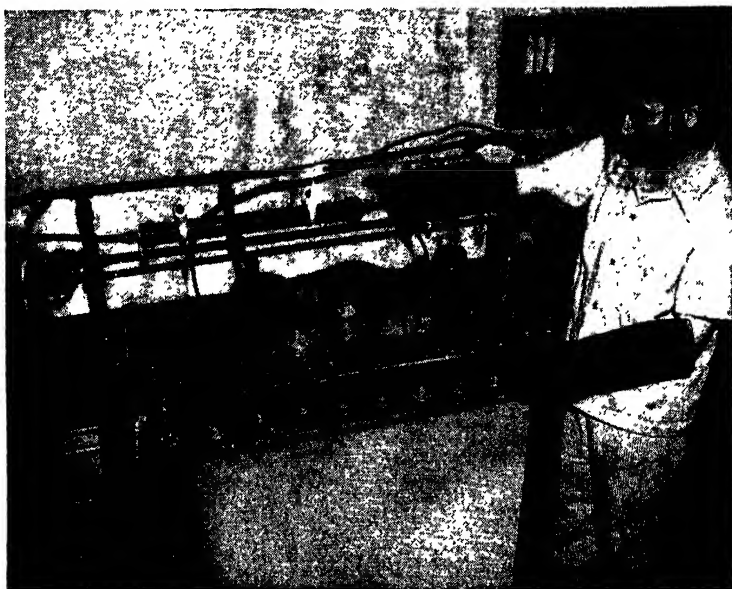
FIG. 145. A 250-amp fluorine cell. (*Pennsylvania Salt Manufacturing Company.*)

chiefly by the anode life and averages 200,000 amp-hr. Operation results in the conversion of KHF_2 to KF. Regeneration is accomplished by the batchwise introduction of gaseous hydrogen fluoride through inlets for the purpose. Operating details are given in Table 66 under the high-temperature heading.

Approximately 2.8 to 3.0 kwhr per lb of fluorine is required for the preferred 100°C cell.

Operational details[24] of German fluorine production at Falkenhagen and at Leverkusen are given in Table 66. German practice made considerable use of elektron magnesium alloy

[24] NEUMARK, H. R., *Trans. Electrochem. Soc.*, **91**, 367–385 (1946).

as a material of construction for cell bodies, diaphragms, and other cell parts.

Electrolysis of Sodium Sulfate. Sodium sulfate is produced in large quantities as a by-product of rayon manufacture as the result of precipitation of cellulose from alkali solutions by sulfuric acid. The conversion of sodium sulfate back to sodium hydroxide and sulfuric acid has intrigued many inventors. The preferred procedure is an electrochemical one.

Graphite, so useful in chloride electrolysis, is attacked and disintegrated in sulfate solutions. Corrosion studies indicate that soft lead as well as hard lead was not completely satisfactory, but lead-silver alloys showed promise. Studies in nonflowing electrolytes[25] indicated that 7.5 to 10 per cent silver-content lead alloys showed reasonable service life at 40 to 50°C, but attack was greater above this point. The alloys are sensitive to the presence of moderate amounts of chlorides, but sodium sulfate from viscose manufacture is almost free of chlorides.

Sodium sulfate electrolysis requires diaphragms even with mercury electrodes. The diaphragms have to be resistant to the electrolytic products, to the alkaline reaction on the cathode side, to the sulfuric acid on the anode side, and to oxygen and ozone from the anode process. The hydrogen formed at the cathode should not get into the anode space in the form of very small gas bubbles. The diaphragm must also have sufficient mechanical strength and stiffness, if it is to be used horizontally or vertically.

Microporous rubber and synthetic ceramic materials were found suitable. The best cell for sodium sulfate electrolysis was one with vertical mercury cathode and lead—10 per cent silver alloy anode using a diaphragm of microporous rubber. Mercury flows down the inner surface of the steel body. At 1,000 amp per m^2, 40 to 50°C, the voltage is 4.4. Products are 50 per cent NaOH and 250 g per liter H_2SO_4 containing 230 g per liter Na_2SO_4.

The rate of flow through the diaphragm has an effect on the current efficiency, which first increases with the rate of percolation of the electrolyte through the diaphragm and then approaches a limiting value. With a more concentrated sulfate

[25] GARDINER, W. C., Tech. Industrial Intelligence Branch, U.S. Department of Commerce, *FIAT Final Rept.* 831 (PB 34,812), June 17, 1946.

solution, the current efficiency is high with lower rates of flow. If more concentrated solutions are electrolyzed with a lower rate of circulation through the cell and diaphragm, the degree of conversion does not increase as much because of the higher concentration at the start. In the anolyte, a sulfuric acid concentration as high as possible is desired in order to reduce the cost of concentration and purification. The current efficiency decreases with higher sulfuric acid concentration in the anolyte.
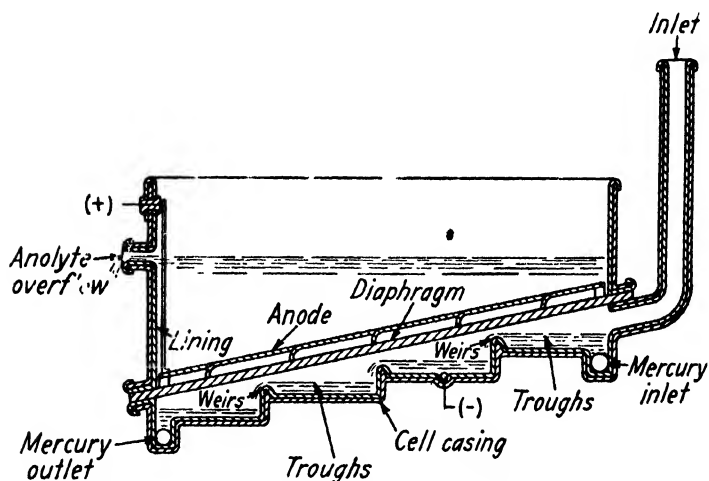
FIG. 146. Aten mercury cell for sodium sulfate electrolysis.

In order to lower the voltage, very high sodium sulfate concentrations are used in the electrolyte for mercury cells, because with that type of cell the solution in the cathode compartment does not become strongly alkaline and, therefore, precipitation of sulfate cannot occur.

Operating data for various cells are given in Table 67. Figure 146 shows a cell construction of an American experimental cell proposed by Aten.

The current densities are about half as high as in alkali chlorine electrolysis; otherwise the voltage and energy expense are too high because a diaphragm is necessary and the electrolyte has a considerably lower conductivity, especially at the lower temperatures.

While the current density of 1,000 amp per m² seems to be

low compared to the density of the alkali-chlorine electrolysis, the cell voltage is much higher than that of alkali-chlorine electrolysis (5.5–6 volts against 4–4.5 volts). Because alkali-chlorine electrolysis gives a useful anode product, the sodium hydroxide from the sulfate electrolysis must carry one and one-half times the energy cost compared to the sodium hydroxide from NaCl.

TABLE 67. SODIUM SULFATE ELECTROLYSIS

	Iron cathode, two-diaphragm cell	Aten cell	Mercury cathode, one-diaphragm cell	
			Horizontal	Vertical
Electrolyte concentration, density	1 2–1 25		1 3	1 3
Caustic soda, NaOH, g/l	125		550–600	550–600
Na$_2$SO$_4$, g/l	150			
Anolyte, H$_2$SO$_4$, g/l	150–160	10–15%	240–260	240–260
Na$_2$SO$_4$, g/l	150	13%	200–220	210–240
Temperature, °C	70		40–50	40–50
Current, amp			9,000	
C.d., amp/sq ft	93	100–250	93	93
Amp/m^2	1,000	1,075–2,688	1,000	1,000
Voltage	5–6	5 5–7	5 5–6	4 4
Energy consumption: Kwhr/lb NaOH	2 27–2 73		1 77–1 93	1 41–1 55
Kwhr/100 kg NaOH.	500–600		390–425	310–340
Current efficiency, %	70–80	90–97	95–97	95–97
Cell material		Glass-lined iron, or wood	Steel	
Cell size, length × width			27.88′ × 3.28′ (8.5 m × 1 m)	
Anode material.	.	Perforated sheet lead	Pb-Ag alloy (7.5–10% Ag)	Pb-Ag alloy
Cathode material	Iron	Mercury	Mercury	Iron or nickel, coated with mercury
Cathode size	. .	.	.	7.8″ diam × 5 9′ (20 cm diam × 1.80 m long)
Anode-cathode spacing	. . . .	0.7 in. (17.78 mm)	0.394 in. (10 mm)	0.315 m. (8 mm)
Diaphragm material	. . . .	Porous ebonite	Mipor (micro-porous caout-chouc)	Mipor
Cell products: Sulfate-free caustic, %	.		50	50
H$_2$SO$_4$ in anolyte, %	.. ....	. . .	20+	20
Na$_2$SO$_4$, %...	.		15–12	16–19

Large units were made with round cathodes in a vertical cell. The cathode surface covered with mercury is cylindrical. Fig-

ure 147 shows a schematic drawing of the vertical sulfate cell in which the cathode is also the side of the vessel. The cathode is irrigated from a ring-shaped mercury overflow. The mercury leaves the cell through a trap. In the interior a cylindrical anode of lead-silver alloy is arranged. It is covered with a Mipor diaphragm and perforated to facilitate the passage of the electrolyte. The evolved oxygen is drawn off on the upper
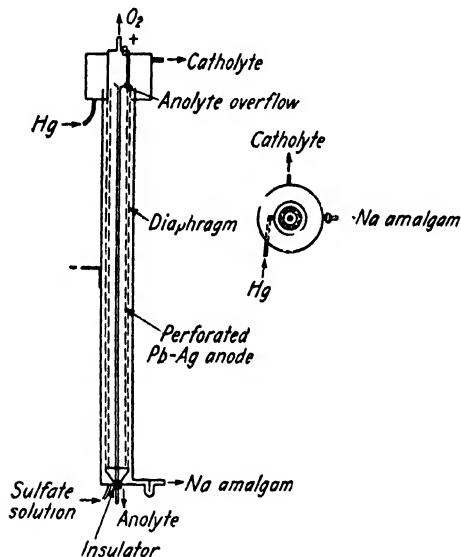
FIG. 147. Vertical mercury cell for sodium sulfate electrolysis.

end of the anode space. The sulfate solution flows in at the bottom of the cell, and a part passes through the diaphragm into the anode compartment, from which it overflows in a pipe, while the remainder becomes gradually more dilute as it flows upward between the diaphragm and the cathode side to leave the cell as catholyte to be resaturated. By this countercurrent flow of electrolyte and mercury, the amalgam flow is stabilized around the whole surface of the round cathode, permitting greater heights of the cathode to be covered with a film of downward-flowing mercury.

Large cells had an effective height of cathode of 1.80 m (5.9 ft), a diameter of 20 cm (7.87 in.), a cathode surface of about 1.1 m² (11.8 sq ft). The cell could normally be loaded with 1,000 to

1,100 amp (current density of 1,000 amp per m² or 93 amp per sq ft) and would still work with one and one-half times this current. The cell rests on four insulators. The anode cylinder carrying the anode bus extends out of the cell. The cathode compartment is open, but the anode compartment is covered because it must be kept under suction.

The concentrated amalgam leaves through a circular trap surrounding the cathode bottom. In the outer compartment of the trap compartment the mercury rises higher than in traps of horizontal cells in order to compensate for a higher electrolyte column. The amalgam then passes to the decomposing tower. On the bottom of the cell are also the electrolyte inlet and the anolyte outlet.

The products of electrolysis were the same as those of the horizontal cell: 50 per cent sulfate-free caustic soda liquor, an anolyte acid with about 20 per cent H_2SO_4, and 16 to 19 per cent sodium sulfate, oxygen from the anode chamber, and hydrogen from the amalgam decomposer. The current efficiency was as high as with the horizontal cell, 95 per cent and more. The voltage was in the region of 4.4 volts, at a current density of about 1,000 amp per m² (93 amp per sq ft) compared to 5.5 volts with the horizontal cell. This improvement is caused by the reduced resistance. The distance between cathode and diaphragm can be reduced several millimeters with the vertical cell compared to an average of 10 mm (0.39 in.) with the horizontal cell. With this lower voltage the energy consumption amounts to four-fifths of the value for the horizontal cell, 3.1–3.4 kwhr per kg (1.41–1.55 kwhr per lb) of NaOH.

CHAPTER 18

HYDROGEN AND OXYGEN

Commercial hydrogen and oxygen cells are built entirely of iron or steel, insulating materials, and asbestos cloth for diaphragms. Every effort is made to have simple and inexpensive construction. Care is taken to reduce all contact voltages to a minimum so as to obtain the lowest possible cell voltages. Cells are so well designed that almost theoretical yields of the gases are obtained. The electrolyte ordinarily employed is an alkaline solution of either 15 to 20 (sometimes as high as 30) per cent NaOH or its equivalent KOH.

Except in regions where power is very cheap, hydrogen production is carried on at low cost by methods involving the utilization of steam and iron or water gas or natural gas. In industrial centers oxygen may be more cheaply manufactured by liquid air methods. For certain industrial operations, very high purity hydrogen is required, as, for example, in the hydrogenation of oils to produce solid fats where ordinarily electrolytic hydrogen is preferred. Many electrolytic hydrogen installations have been economically possible only where hydrogen of high purity was desired and the by-product oxygen could be profitably disposed of. The situation is somewhat different, however, in isolated localities where cheap power is available. Very large installations of electrolytic hydrogen plants have been made in regions of cheap power located at considerable distances from industrial centers where the hydrogen is employed for fixation of nitrogen as ammonia by pressure processes, which in turn is employed in the manufacture of fertilizers.

Types of Cells. All the important industrial cells are of the diaphragm type but differ in the arrangement of their electrodes, diaphragms, external containers, gas outlets, and assembly in batteries./The I.O.C. unit tank, the Levin or Electrolabs and its successor the Gas Industries generator, the Knowles, and the filter-press type of cells will be described. A large number of

I.O.C. cells are in use, but the unit is no longer manufactured. A similar situation holds for the original Levin cell. The units in commercial operation produce pure gases, the oxygen being 99 per cent or better and the hydrogen 99.5 per cent or better, at current efficiencies approaching 100 per cent. The voltages on the cells are the summation of the decomposition voltage of water (1.23 at room temperature), the oxygen and hydrogen overvoltage, plus those necessary to overcome the electrolyte resistance and the ohmic resistance of the electrodes, contacts, and terminals. In all cases the raw material for electrolysis is distilled water. In continental Europe there have been developments of nondiaphragm cells and equipment for electrolysis of water under pressure.

Unit Generators. The details of construction of the I.O.C. unit generator are shown in Fig. 148. It consists of a cast-iron body divided into two vertical compartments by means of an inner diaphragm of woven asbestos. A nickel-plated cast-iron anode is located on one side of the diaphragm and insulated from the cast-iron body, the cast-iron cathode being located in a similar position on the other side. A reservoir for the electrolyte is cast as an integral part within the head of the generator body. The same holds true for the outlets for oxygen and hydrogen. A simple arrangement of chambers and water seals acts as an automatic internal-pressure equalizer. The entire unit stands on two insulating bases. Individual units are about 3 ft 6 in. wide, 7 ft high, and about 4 in. thick. Cell voltages, depending upon the number of units connected in series, are from 2.2 to 2.5, the current per cell being 600 to 1,000 amp. In practice it is usual to arrange the units in batteries of 5 to 60 cells electrically connected in series.

The Levin or Electrolabs cell is also of the unit type, its construction being shown in Fig. 149. The body of the cell consists of two sheet-metal frames between which is an asbestos diaphragm. Anolyte and catholyte compartments contain the nickel-plated sheet-steel anode and· the cobalt-plated sheet-steel cathode, respectively. Both platings were made to reduce overvoltage. Each compartment of the cell has an independent water feed which serves as a blowoff device to vent the gas from each compartment under abnormal conditions. The 250-amp cell is 30 by 25 by $6\frac{1}{4}$ in., weighing 145 lb and having a produc-
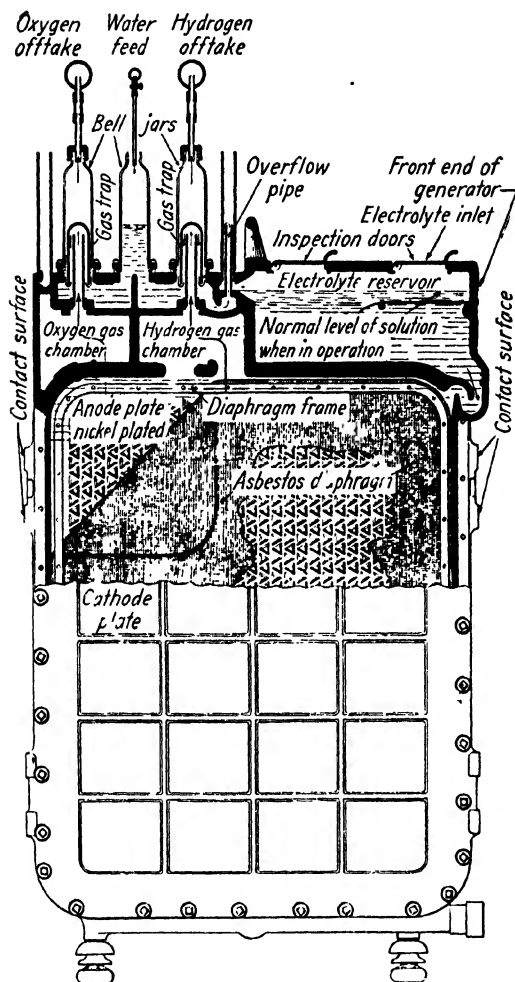
Fig. 148. Sectional view of I.O.C. unit generator.

tion of 4 cu ft of hydrogen per hour; the 600-amp unit is 43 by 37 by $8\frac{1}{2}$ in., weighing 325 lb and having a capacity of 9.6 cu ft of hydrogen per hour. The cell members are welded together and rigidly assembled. In practice, units are connected in batteries electrically in series.

The Electric Heating Equipment Company unit generator is a development of the original Levin cell, embodying most of the
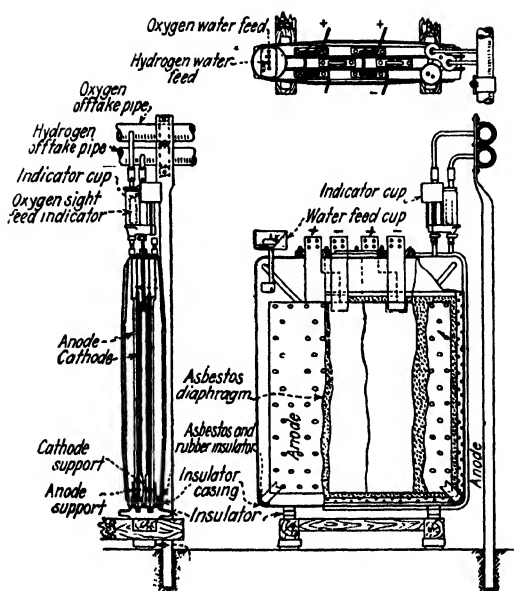
Fig. 149. Structural details of Levin cell.

structural features of the Levin anode and cathode. These are made in capacities of 500, 1,000, 1,200, 2,000, and 5,000 amp. The most common size is the 1,000- or 2,000-amp unit producing 15.9 and 19 cu ft of hydrogen per hour at their respective ratings and 2.1 volts resistance.

The gas analyses are: oxygen 99.6 to 99.7 per cent and hydrogen 99.95 per cent plus.

The cell is simply constructed of heavy electrodes and current-carrying members with a convenient assembly for renewal of insulation and cleaning. Installations have run 9 years before any overhauling, but 5 to 7 years is general. The cell construction is shown in Figs. 150 and 151. The anode and cathode are located on opposite sides of an asbestos diaphragm dependent from a cover closing the welded sheet-steel tank which serves as container for the unit. A typical cell room is shown in Fig. 152.

Knowles Cell. The Knowles cell consists of a sheet-steel tank in which are immersed anodes and cathodes underneath sheet-steel gas-collecting bells. Alternate electrodes are surrounded by asbestos diaphragms which are hung from and supported by

the sheet-steel bell above that electrode.   The construction of the cell is shown in Fig. 153.   The electrodes are of heavy steel plate at least ⅛ in. thick.   They are hung from the collecting bells but electrically insulated from them.   The electrical connections of adjacent electrodes are staggered.   Hydrogen and oxygen are taken off at the top of alternate collecting bells. A number of these units are assembled in a rectangular tank and a skirting or tank diaphragm provided around the inside of the tank.   The bells, which in turn carry the electrodes and the diaphragms, are themselves carried on the edges of the steel container. A typical small Knowles cell installation is shown in Fig. 154.

Fig. 150.   Unit generator for H_2 and O_2.   *(Gas Industries Company.)*

The electrolyte is generally an 18 to 20 per cent NaOH solution, although a number of plants employ a 25 to 30 per cent KOH.   With the latter, the production of gases per kilowatthour

ANODE ASSEMBLY   ASBESTOS CURTAIN AND COVER ASSEMBLY   CATHODE ASSEMBLY
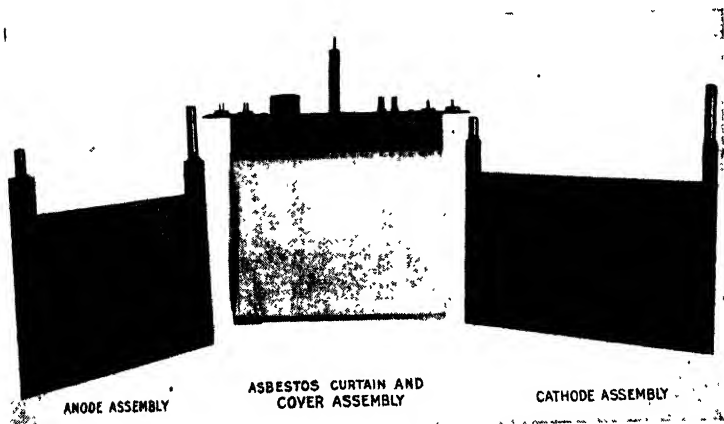
Fig. 151.   The major parts of a unit generator.   *(Gas Industries Company.)*

is slightly higher, but the electrolyte is much more costly.   Experience has shown that the diaphragms and insulators are not so durable with KOH as with NaOH.   The anodes are given a mat surface and coated heavily with nickel.   With ordinary care they have an operating life of 10 years.   The diaphragms are sewn on strips of iron which are forced up between adjacent gas bells and secured there, making a gastight joint.   They hang down loosely between the electrodes and extend a considerable

Fig. 152.   Electrolytic gas plant for H_2-O_2 production.   (*Electric Heating Equipment Company.*)

distance below the lower edges.   They are thus under no strain and float freely in the electrolyte.   The gas offtakes are S-shaped pipes with glass tubes placed in them as insulators.   In operation the temperature of the cell is controlled at 60 to 65°C.   A typical Knowles 3,000-amp cell would be 4 ft 1 in. long, 2 ft 5 in. wide, and 2 ft 7 in. deep, operating at a voltage of 2.125 to 2.25, producing 48.4 cu ft of hydrogen per hour at the rate of 7.6 cu ft of hydrogen per kilowatthour, the corresponding figures for oxygen being half of these.   The hydrogen purity is 99.75 and
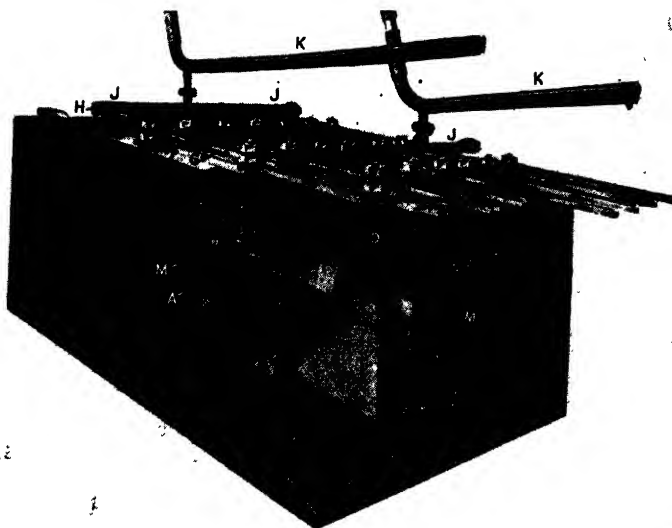
Fig. 153. Sectional view of Knowles cell.

AA	Electrodes	*GG*	Copper connections
BB	Gas-collecting bells	*HH*	
CC	Electrode leads	*JJ*	Gas-collecting pipes
DD	Sealing and safety tubes	*KK*	Gas offtake pipes
EE	Insulating tubes	*LL*	Asbestos diaphragms
FF	Top insulators	*MM*	Skirting

Fig. 154. A Knowles plant showing twenty 2,166-amp cells. (*International Electrolytic Plant Company.*)

oxygen 99.5. Figure 155 gives the current-voltage relation for a 3,000-amp cell designed to operate at 2.25 volts. The current efficiency of the cell is more or less constant, irrespective of load, so that the power consumption per unit of gases varies as the voltage. Figure 156 shows the relation between power consumption and cell voltage.

In contradistinction to the unit cells of the I.O.C. and Levin types, numbers of sets of anodes and cathodes in the Knowles cell are in parallel in the containing tank, and electrical connection is then made so that the entire group is in series with other similar groups.

Trail Cell.[1] This cell has a concrete top which is a casting comprising the gas-
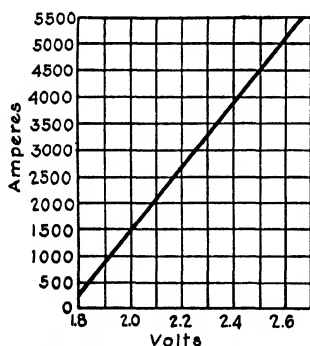
Fig. 155. Current-voltage curve of a 3,000-amp Knowles cell.
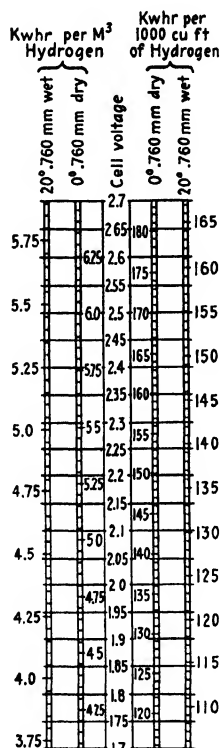
Fig. 156. Relation of power consumption to voltage in a Knowles cell.

collecting bells and gas chambers, the electrode supports and insulators, and the cell cover, which in earlier hydrogen cells of the tank type were all separate items. To this concrete top are attached the electrodes, the asbestos diaphragms, the outer asbestos collecting skirt, the feed-water system, and the

[1] SUTHERLAND, B, P., *Trans. Electrochem. Soc.*, **85**, 183–191 (1944); COLLS, E. A. G., MOORE, A. W., and MORRIS, D. D. (to Consolidated Mining and Smelting Company), U.S. Patent 2,293,594 (Aug. 18, 1942).

busbar and gas main connections. When the assembly is fitted onto the steel cell tank, it forms a complete cell for the production of hydrogen and oxygen.

In a general sense, the electrode, diaphragm, and general arrangement are somewhat similar to the Knowles cell, but metal gas-collecting bells are eliminated.

The cell top is made entirely of reinforced concrete and is in the shape of a rectangular box divided by a 5-in. (13-cm) thick vertical partition into two equal compartments serving, respectively, as hydrogen- and oxygen-collecting chambers.

Directly above each electrode and parallel to it there is in the concrete, which forms the floors of the two gas chambers, a "slot" or long, narrow, inverted trough which serves as a gas-collecting bell. One-half of the length of each slot or trough is closed in above with a sloping ceiling which constitutes a section of the floor of the gas chamber immediately above. Over the other half of its length the slot is open into the other gas chamber. As the slots after assembling are alternately over anodes and cathodes, thus collecting, respectively, oxygen and hydrogen, they are open alternately on one side and the other feeding the gas into the appropriate gas chamber. The oxygen and hydrogen, kept from mixing by means of asbestos diaphragms, are thus caught in the collecting bells and pass through the openings or ports into their respective chambers.

The operating details of these large H_2-O_2 cells of 10,000-amp capacity are given in Table 68.

Cell Capacity. Manufacturers of H_2-O_2 cells do not talk in terms of current density in reference to anodes and cathodes, in that the term is misleading in this connection. Knowles states[2] that during the early stages of research in connection with the manufacture of cells, it was discovered that current density is not controlled by plate area. This seems contrary to theory. If, however, the width of an electrode be doubled, its capacity is doubled; but if the depth of an electrode be doubled, its capacity is not similarly affected in that the upper portions of the deeper electrode are in contact with an electrolyte of higher resistance as the result of the larger volume of gas mixed with the electrolyte in this area. Similarly, in actual practice it has

[2] Private communication from A. Edgar Knowles, International Electrolytic Plant Co., Sandycroft, Chester, England.

TABLE 68. OPERATING DETAILS OF TRAIL H_2-O_2 CELLS (10,000-AMP CAPACITY)

Electrolyte.....	28% KOH
Temperature, °C....	. 75
Tanks:	
Material of construction.... ..	Steel 0.16 in. (4 mm) thick
Length × width × depth	$3\frac{1}{2}'$ × 2' × 4' (107 × 61 × 122 cm)
Number of electrodes........	. 15
Floor space per cell... ..	. 18 sq ft (167 dm²)
Amperage.......... .. .	. 10,000
Voltage......	. 2.25
C.d., anode....	67 amp/sq ft (7.2 amp/dm²)
Electrode spacing, face to face.	1.3 in. (33 mm)
Anodes:	
Material....	Nickel-plated steel 0.3 in. (7.6 mm) thick, 0.003-in. nickel
Size........	. 39" × 39" (99 × 99 cm)
Number......	7 .
Cathodes:	
Material..... .	. Steel, 0.3 in. (7.6 mm) thick
Size..... .	. 39" × 39" (99 × 99 cm)
Number.. .	.. 8
Anode diaphragms:	
Material..... ..	Asbestos cloth 0.1 in. (2.5 mm) thick, 1% cotton
Weight...	. 0.36 lb/sq ft (17.6 g/dm²)
Arrangement.	Around each anode
Life... . . .	. . 10 years
Cathode diaphragms:	
Material... .	Same as anode diaphragms
Weight... .	Same as anode diaphragms
Arrangement. .. .	As curtains or skirts around all cathodes (complete assembly)
Life........	10 years
Gas-collecting chambers...........	Concrete, 1 part cement, 1 part 99% SiO_2
Purity of products:	
Hydrogen, %..................	99.9
Oxygen, %....................	99.6

been found that resistance of the electrolyte between two opposite poles is not in proportion to the distance between these poles, in that as the poles are brought nearer, the intervening electrolyte has a greater number of gas bubbles in it. In the case of cells with electrodes having numerous points or projections cast on them, they were originally assembled with the

points almost touching the diaphragm. It was found that, if these electrodes were placed ½ in. farther apart, the resistance was actually reduced instead of being increased. When electrodes having projections on them were studied in glass tanks, it was found that gas production was concentrated on those points closest to each other and that recesses on the electrodes hardly produced any gas. If current density were calculated on the effective area exposed by the corrugations or raised surfaces, the current density would be very high; but if all the area of such an ornamental type of electrode be considered, the current density would be absurdly low.

Filter-press Cells. The plate-and-frame filter press with recessed plates has been modified to serve as a H_2-O_2 generator, where asbestos diaphragms take the place of filter cloths. The design is employed for small laboratory units to be operated on standard line voltages. The plates are bipolar electrodes made of slightly corrugated cast iron which is nickel-plated. The diaphragms are of asbestos with rubber gaskets which serve as insulators between adjacent plates. Each plate except the end ones has three holes, one on each side at the top to lead off the two gases, and one at the bottom for the electrolyte. In the laboratory cells built in the United States the electrolyte is a 20 to 30 per cent NaOH. A sufficient number of plates are connected together so that, depending upon the load, when 2.0 to 2.5 volts are used per compartment, the unit may be operated on a 110-volt circuit. Each compartment connects through channels, similar to those in a plate-and-frame filter press, to a central offtake for oxygen and hydrogen which pass out through sight glasses, and the pressure on the two sides of the diaphragm can be equalized. Under careful operation hydrogen purity does not fall below 99 per cent, being closer to 99.5. This type of unit has found commercial application where only small quantities of hydrogen are desired.

In Europe there has been a development of the filter-press type of cell employing metallic diaphragms, the units being of large size. As the result of different economic conditions and the employment of electrolytic hydrogen in connection with ammonia synthesis, electrolysis of water has been more widely employed in Europe than in the United States. As a result the subject has been more extensively studied and a number of differ-

ent types of cells of large capacity have been developed and used.

The tank type of H_2-O_2 cell was criticized because of its comparative bulkiness, relatively large floor-space requirements, as well as its inability to be connected up to standard voltages except in series. The filter-press type of cell, either operating under normal pressures or operating under increased pressures, was held up as a model. Weakness of diaphragm and failure of diaphragms in service were serious objections. These objections were supposedly entirely overcome by perforated sheet-metal diaphragms, an example of which was the perforated sheet metal of the Pechkranz cell in an installation of 300 cells taking 108,000 kw. This installation was followed by another one, but not so large, at the plant of the Consolidated Mining and Smelting Co. at Trail.[3]

The Pechkranz electrolyzers can be operated at from 2 to 2.5 volts per cell, and up to 150 cells can be built in one electrolyzer. Two units of 140 cells in series can take 700 volts and up to 2,500 amp. Each unit will absorb 875 kw and yield over 5,500 cu ft of hydrogen per hour, at power consumptions of the order of 125 to 170 kw per 1,000 cu ft of hydrogen, depending upon the percentage load. Circular iron sheets constitute the electrodes, and 25 per cent KOH is used as electrolyte.

The feature claimed for the Pechkranz cell was the perforated diaphragm. Surging of the electrolyte markedly damaged the nickel diaphragms, so that they proved to be too fragile for continued use and were subjected to material alterations for successful operation.

A typical large-scale filter-press type of electrolyzer employing metal diaphragms is shown in Fig. 157.

Electrolysis under Pressure. An interesting phase of this development is pressure electrolysis of water. In contradistinction to normal operation under slightly greater than atmospheric pressure, the water is electrolytically dissociated under pressures as high as 200 atmospheres, or approximately 3,000 lb. Since the confining space does not change while the amount of gas constantly increases, the pressure will continue to rise. A large amount of time and effort has been spent in an endeavor to promote pressure electrolysis, since inventors sensed an opportunity for saving compressors.

[3] ELWORTHY, R. T., *Chem. & Met. Eng.*, **38**, 714 (1931).

As in electrolysis under atmospheric pressure, one-third of the gas volume consists of oxygen and two-thirds of hydrogen. The quantities generated are proportional to the current; and as long as the pure gases are separated as produced, the quantity is practically independent of the nature of the equipment. The chief difficulty encountered was the economic production of sufficiently pure gases, while problems of construction, such as strength of materials and the prevention of leakage, were likewise
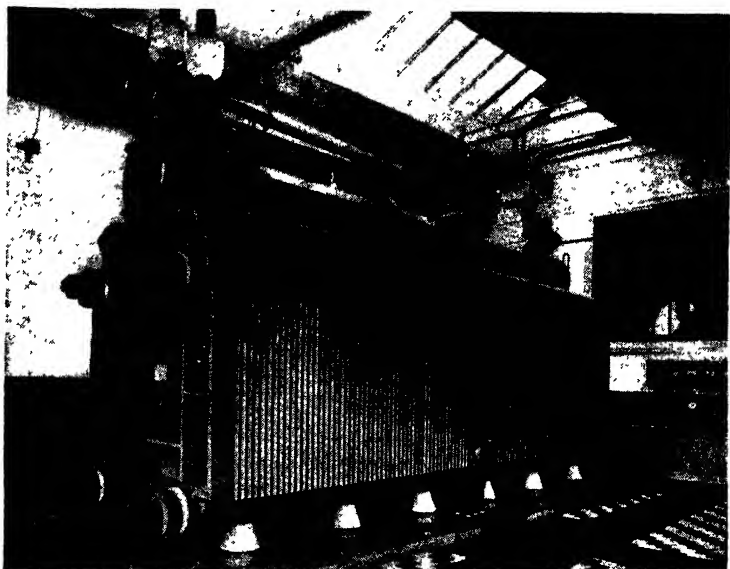
FIG. 157. Type C200 Bamag H_2-O_2 electrolyzer, 8,500 cu ft of hydrogen per hour at 5,360 amp and 216 volts. (*Albert H. Bruecke.*)

to be considered. Insulation was another factor, particularly for an arrangement of cells in series.

In experiments on a laboratory scale little trouble was experienced in maintaining the purity of gases with low voltages, provided the apparatus was absolutely tight and the gases were kept in a strict 2:1 ratio. In practice, however, these conditions were not so easily maintained because arrangement in series is necessary for normal voltages but difficult for pressure electrolysis due to leakage. Furthermore, an even removal on both sides, necessary to avoid changes in the volume ratio, is not easily accomplished. At 200 atm, for example, a difference in pressure

of only 5 per cent will result in a net pressure of 10 atm on the fragile separating walls. In pressure cells where the arrangement of the electrodes affects the separation, the gas under higher pressure forces the electrolyte to the opposite part of the cell. In addition the heat and gas bubbles may cause motion and mixture of the electrolytes and the entrained gases.

Pressure Cells. A typical electrolyzer is given in Fig. 158. The tubes indicated by *A* are the actual pressure cells, through

A- Pressure cell
B- Current entering electrode
C- Cover
D- Distributor
E, F- Valves to gas holders
G- Oxygen holder
H, I- Hydrogen holders
K, L- Tubes to cylinders
M- Compensating line
N- Replacement water feed
O, P- Check valves
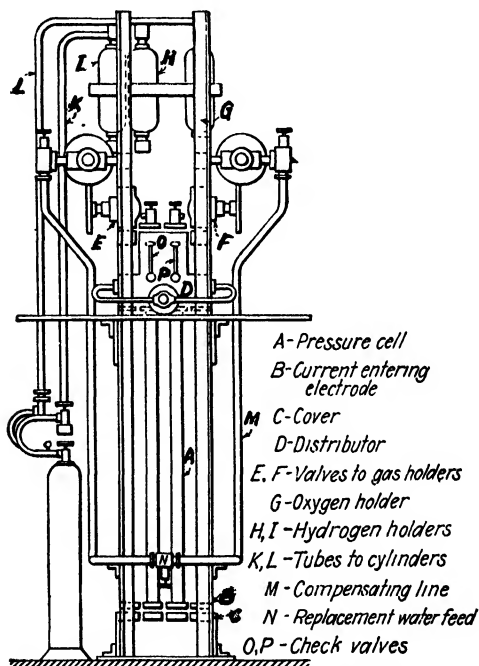
FIG. 158. Design of electrolyzer producing gas at 150 atm pressure.

the axis of which run the negative nickel electrodes generating the hydrogen. Each of the latter is surrounded by a concentric separating wall, the walls in turn being surrounded by concentric positive electrodes which generate the oxygen. The electrolyte used is KOH. Current is supplied to the positive electrodes at *B*, the vessel itself serving as conductor. The current passes through the separating wall (not shown) to the negative electrode, leaving the cell at its cover *C*. For operation at normal voltages the cells are arranged in series in a certain definite order.

The oxygen rises up along the outer section of the pipe A, collects in the passages of the distributor D, then enters the holder G by valve F, and finally flows to the cylinders through the pipe L. Completely separated from the oxygen by the intervening wall, the hydrogen rises along the axis of A, collects in the other passages of the distributor D, and flows through the valve E to the holders H and I and through the pipe K to its cylinders.

The two electrolyte chambers are connected by a compensating line M, to which the replacement water for the electrolyte is fed at N. This compensating line has a large capacity in order to prevent one-half of the electrolyte from running into the other when there is a difference in pressure. Its great length allows of such a small cross section, however, that the velocity of the feed water for the electrolyte greatly exceeds that of the gases tending to enter the compensating line. This is the first application in pressure cells of an elastic compensation which will react to the slightest variations in pressure. A special device is also provided to bring the various elements back to a state of equilibrium. The check valves O and P serve to cut off the cells from any unlooked-for difficulties arising outside.

The energy consumption of a pressure electrolyzer is from 3 to 3.5 kwhr per m³ of hydrogen at 20°C and 760 mm of mercury. In tests the purity of 98 per cent was exceeded, 99.1 per cent oxygen and 99.8 per cent hydrogen being produced.

In operation the cells are first subjected to a higher voltage than that necessary for decomposition. A current begins to flow which increases with rising voltage and the cylinders to be filled are connected. When the desired pressure of 150 or 200 atm has been obtained, the cylinders are removed and new ones connected, and the pressure drops again corresponding to the volume.

The relation of current and voltage in a cell for different pressures and temperatures is given in Fig. 159. It is evident that at rising pressures dissociation requires lower voltages than at atmospheric pressure, and furthermore that the pressure rise reduces the voltage more than the higher temperature alone. A saving is thus effected not only in compressors but also in the energy required as compared with ordinary dissociation, since the voltage drop is a measure of the energy consumption.

The minute gas bubbles formed at the electrodes have such a tremendous surface tension that the 150- or 200-atm pressure in the gas chambers becomes insignificant in comparison. Hence the difference in the energy required to produce the gas at normal and at the higher pressure is slight. On the other hand, it was
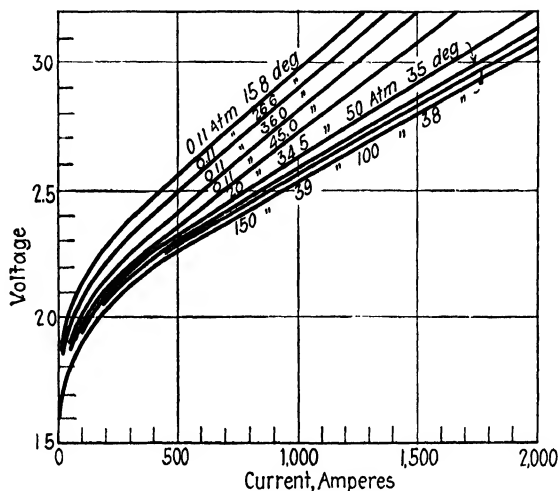
FIG. 159. Variation of current with voltage in a cell at different pressures and temperatures.

found that the liberated gas bubbles which affect the electric path are compressed as the pressure increases and because of their reduced volume lower the electrolyte resistance. Similarly the polarization due to the bubbles that adhere to the electrodes is reduced as the pressure rises. These reductions of the electrode voltage in pressure electrolyzers outweigh the opposite factors, so that the total voltage decreases with a rising pressure.

ELECTROLYSIS OF FUSED SALTS

Molten salts are good conductors of electricity, and their conductivity is of an electrolytic nature. The anode and cathode products are analogous to those from aqueous solutions. Thus $PbCl_2$ gives lead and chlorine, NaCl gives sodium and chlorine, $NaNO_3$ gives sodium together with oxygen and nitrous gases.

The conductivities of molten salts are considerably greater than the conductivities of the same salts in aqueous solution. The conductivity of a number of fused electrolytes and the variation with temperature are shown in Fig. 160. It can be seen that the effect of temperature is to increase conductivity as a straight-line function. Increase of temperature decreases ✓ viscosity, and conductivity varies inversely with viscosity in✓ most cases. Conductivities of fused salt mixtures do not usually follow the straight line connecting the two components, but deviate from the mixture law.[1] Figure 161 for KCl, NaCl, and $CaCl_2$ mixtures shows that the combinations have appreciably higher resistances or lower conductivities than the components. Measurements of these values do not involve difficulties, as the procedure is similar to that employed for resistance measurements.

Current Efficiency. The validity of Faraday's law for the electrolysis of molten salts has been rigorously proved.[2] The factors which lower current efficiencies under ordinary conditions are of greater importance at high temperatures. Chemical reaction velocity is higher, and diffusion is markedly increased. Anode and cathode products must be prevented from mixing, and be restrained from reacting with the gases of the atmosphere as well as the electrolyte; otherwise lowered current and energy efficiencies will result. Major sources of losses of electrode

[1] SANDONNINI, C., *Gazz. chim. ital.*, **50**, I, 289 (1920).
[2] LORENZ, R., and HELFENSTEIN, A., *Z. anorg. Chem.*, **23**, 255 (1900); RICHARDS, T. W., and STULL, W. N., *Z. physik. Chem.*, **42**, 621 (1903).

products are (1) distillation or volatilization or even subliming of metals, which may be reduced by temperature control; (2) mixing of electrode products by diffusion, which may be decreased by employment of diaphragms; (3) formation of metal fog; and (4) reaction with the gases in the atmosphere above the electrodes.
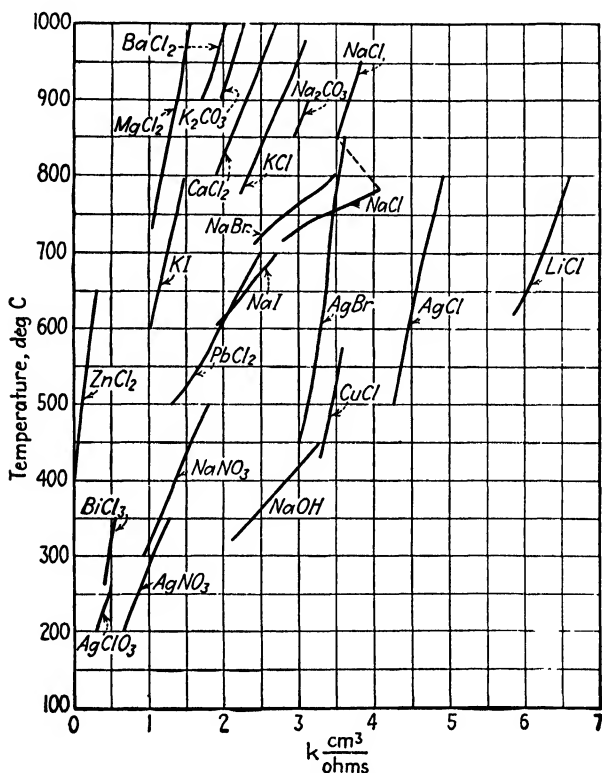
FIG. 160. Electrical conductivity of molten salts and bases.

Current efficiency and yields vary inversely with temperature. When current density is raised, the upward rate of cathode material production is greater than the increase in diffusion which causes loss of electrode products, so that there might be an increase in current efficiency. The value of current efficiency may be zero at low current density if the losses are greater than or equal to the rate of formation of electrode product. The maximum current density is set by heating effects due to electrode-to-electrolyte drop, electrode polarizations and resistance

of the electrolyte, as well as anode effect and metal fog, all of which increase the cell voltage and at times give abnormal values. In unusual cases subsalts may be formed between the metal and the fused electrolyte, or the metal may dissolve in the electrolyte, as in the case of molten NaOH, to form a true solution.

Many base metals may be melted under a covering layer of salts of the metal without solvent effect by the salt on the metal
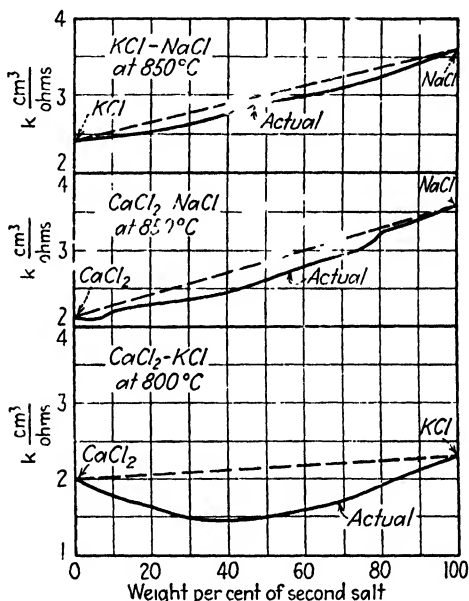
FIG. 161.   Conductivities of salt mixtures in molten state.

itself.   As the temperature is raised, the salt becomes a solvent to a greater or less degree for the metal, the effect reaching an equilibrium point which is a temperature function.   With decrease of temperature, saturation effects cause precipitation of the metal which is in the form of "fog" or clouds.   The "dispersed" metal settles down.   In fused salt electrolysis, metal fog formation may color the electrolyte.   Such a condition is stable only in the absence of contact with massive metal, oxygen, or oxidizing agents, in that the color vanishes when oxidants are introduced, but may be produced or restored by small amounts of reductants.   The metal in fog form is much more reactive (as a result of its finely divided condition) than is massive metal.

Lorenz[3] showed the fogs to be colloidal and contain less than
0.1 per cent metal. Neutral salts[4] prevent fog formation to some
extent, an action which may be measured during electrolysis by
the effect on the cathodic current density.
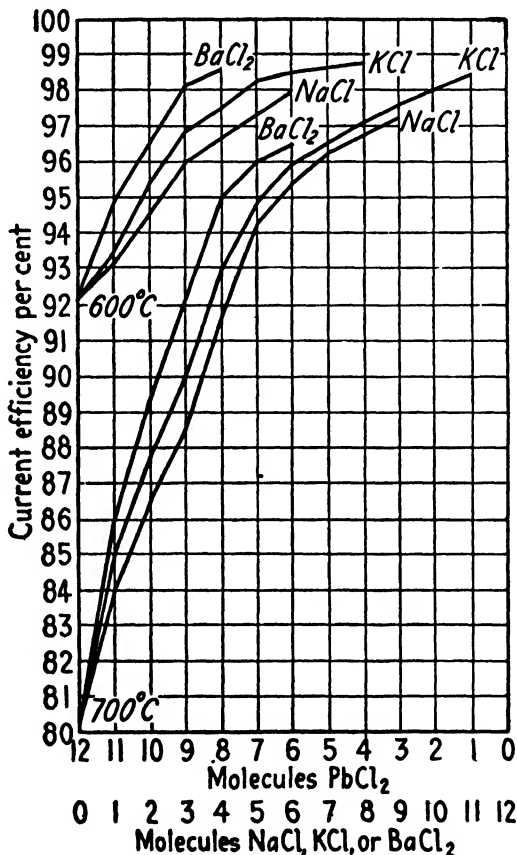
FIG. 162.   Effect of addition of salts to fused $PbCl_2$ on its electrolysis.

Lorenz[5] studied the effect of sodium, potassium, and barium
chlorides on the electrolysis of $PbCl_2$, the results of which are
given in Fig. 162.   The effect of the salt additions is greater at

[3] LORENZ, R., VAN HEVESY, G., and WOLFF, E., *Z. physik. Chem.*, **76,** 732
(1911); LORENZ, R., and EITEL, W., *Z. anorg. Chem.*, **91,** 46 (1915).

[4] LORENZ, R., "Die Elektrolyse geschmolzener Salze," W. Knapp, Leipzig,
1923.

[5] LORENZ, R., *Z. Elektrochem.*, **13,** 582 (1907).

higher temperature where the onset of fog is easier and more persistent. $FeCl_3$ additions lower the yield, but the low boiling point and the decomposition of this salt might also be factors. Appelberg's results of this effect are plotted in Fig. 163.[6] The
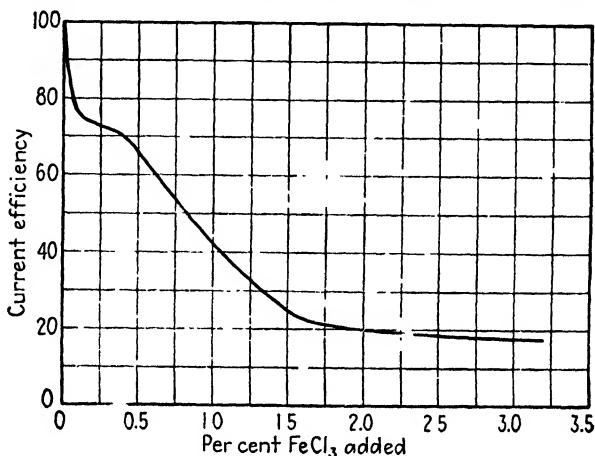
Fig. 163. Effect of $FeCl_3$ additions on current efficiency of $PbCl_2$ electrolysis

anodic oxidation and cathodic reduction of Fe^{++} and Fe^{+++} salts may be a controlling factor.

Decomposition Voltage. In the case of aqueous electrolytes, it has been seen that the emf of the cells depended upon the concentration of the solution. With pure fused salts, questions of concentration do not enter; hence the reversible emf of the cell depends upon the nature of the electrodes, the electrolyte, and the temperature. The decomposition voltage varies in a like manner. Obviously the two values will be equal. With mixtures of salts the emf will depend upon the concentration of the salt corresponding to the metals used as electrodes.

The decomposition voltage for simple fused salts is affected by temperature, higher temperatures with lower viscosities of the salts causing lower decomposition potentials. A number of these are plotted in Fig. 164. Ionization or dissociation of fused salts is a direct function of temperature.

The useful work obtainable from a chemical reaction is measured by the reversible emf of the primary cell employing the reaction. This emf is markedly affected by temperature, a wide

[6] APPELBERG, A., *Z. anorg. Chem.*, **36**, 36 (1903).

range of which is possible with fused salts in contrast to aqueous electrolytes limited by the evaporation or boiling of the solvent. With electrolytic processes corresponding to the reaction fused salt $\rightarrow$ metal $+$ halogen or nonmetal, which is typical of the kind of process employed industrially, the emf or decomposition voltage diminishes as the temperature rises. It would be
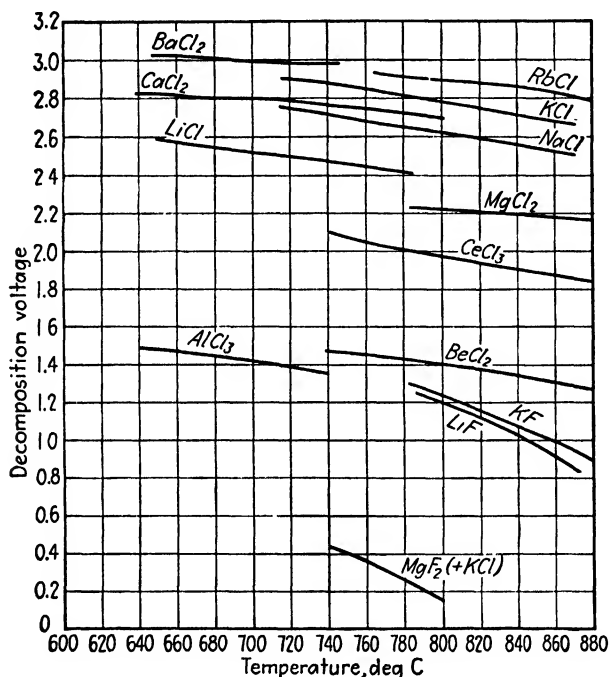
Fig. 164. Variation of decomposition voltage of fused salts with temperature.

advantageous in the electrolysis of fused salts, at least from the viewpoint of the necessary voltage, to employ temperatures as high as possible. With increase of operating temperatures, however, the necessary repair and maintenance charges on the equipment, the increased difficulty of operation, as well as larger heat radiation losses, become increasingly important factors. In addition, decreased current efficiencies would result, as has been shown in previous discussions, with corresponding decreased energy efficiencies and greater power consumption per unit of product.

Polarization and Anode Effect. A troublesome phenomenon known as the "anode effect" often occurs during the electrolysis of fused salts. Without any obvious external cause, the voltage suddenly increases markedly; the amperage decreases; a soft, rustling, hissing sound is heard like the discharge of a small induction coil; and the anode seems to be covered by myriads of little luminous spark discharges. If the anode effect occur with a fairly high frequency, rheostats and busbars in the circuit may rattle and vibrate; if the frequency be high enough, they may give off a musical tone.

During the normal course of electrolysis, the anode is surrounded by gas bubbles which are constantly escaping from it. They appear to form on the anode, break away easily, and escape from the electrolyte. Smooth evolution of gas around the anode is a sign of normal operation. The moment the anode effect occurs, the electrode seems to be entirely surrounded by a film of gas. This covers the surface of the anode and pushes the fused electrolyte away, producing the so-called "nonwetting" of the anode. Small arcs form between the electrolyte and the anode. Complete interruption of the current does not occur, as some current is being carried by these continually shifting arcs. The arcs cause local heating, volatilizing some bath material or producing sufficient gas so that the individual arcs are almost immediately broken. New arcs form, as the bath film near the anode must necessarily be uneven in character, and momentary contacts take place between the anode and bath. This overheating causes very rapid consumption of the anode, which sometimes burns off above the level of the electrolyte, and may cause a lowered yield of product. A very important result of the anode effect is a large unproductive power consumption.

The experimental observations and explanations of those who have studied the anode effect appear complex and confusing.

Assume first that the anode effect is the formation of a gas film surrounding substantial portions of the anode. The film prevents the electrolyte from wetting the anode. The result is observed in the formation of myriads of tiny arcs, since the current must pass from anode to electrolyte through the gas film. Once the gas film has been established, it tends to perpetuate itself, since the arcing generates an excessive amount of localized heat which causes the gas to expand. There is then a consider-

ably higher voltage drop from anode to bath. This involves a greater expenditure of power and tends also to maintain the anode effect.

The factors which interrupt the regular normal evolution of gas at the anode by causing the formation of a high resistance gas film may be many. They may vary from time to time in the same electrolytic operation. Any condition which tends to produce a local overheating on the surface of the anode may start a train of events which results in the anode effect. A high-resistance film of solid material may form on the anode surface. This film may consist of impurities left on the surface of the anode by the continued consumption of carbonaceous material; it may consist of some relatively insoluble constituent of the electrolyte which has migrated to the anode and adhered to it, or it may consist simply of frozen electrolyte which has become attached to the anode through local cooling of the bath.

As this high-resistance film forms, the current density increases in other areas, the voltage drop and the expenditure of power increase, and local overheating may start the formation of an anode effect (gas film) at one or two points. Too high a current density may be an important factor in providing the initial impetus for the anode effect. Moreover, either too hot or too cold an electrolyte may start the anode effect. Too cold an electrolyte may cause freezing on parts of the anode surface, increasing the current density on other parts. Too hot an electrolyte will bring operations into a field which is sensitive to the anode effect.

Surface tension plays a part in the delicate balance between wetting and nonwetting of the anode by the electrolyte. In some cases an electrolyte of high viscosity might permit the retention on the anode of solid material which would start the local overheating.

The anode effect will disappear, of course, when the surface of the anode is cooled, or the current density so reduced that the gas film collapses and the normal evolution of gas is resumed. It will not reoccur until a certain combination of circumstances permits the reestablishment of the high-resistance film.

The anodic current density at which the anode effect begins varies with the type of electrolysis and temperature, ranging from 4 to 5 amp per cm^2 with carbon and 7 to 8 amp per cm^2

with graphite. The phenomenon has been observed with halides of lead, cadmium, silver, the alkali and alkaline earth metals, magnesium, cerium, aluminum; with complex electrolytes of aluminum fluorides, and with commercial electrolytes.[7] Anode effect occurs most readily with fluorides and least with iodides. Halides of carbon are sometimes formed with loss of weight of the anodes.

Just as in aqueous solutions, the various metallic components of a mixture may be separated in the molten state, since the
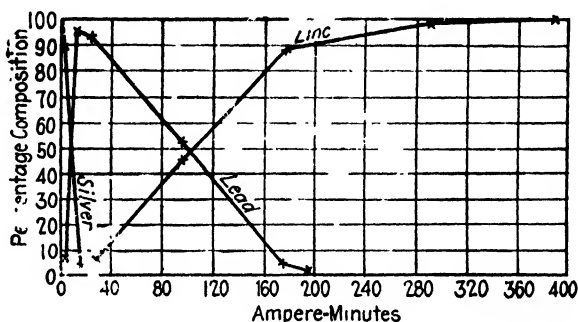
Fig. 165   Relation of composition of cathode products and current during electrolysis of a mixture of fused chlorides of Ag, Pb, and Zn.

different fused salts exhibit differences in decomposition potential. The constituents may tend to alloy among themselves, thus depolarizing each other's discharge and complicating results. Figure 165 shows the results obtained by Lorenz[8] from a mixture of the chlorides of silver, lead, and zinc.   The abscissae represent the quantity of electricity passed since the beginning of electrolysis, and the ordinates the composition of the cathode product removed from the cell at the corresponding intervals of time.

[7] See HULIN, L. P., *Z. angew. Chem.*, **11**, 159 (1898); LORENZ, R., and CZEPINSKI, V., *Z. anorg. Chem.*, **19**, 246 (1899); MUTHMANN, W., HOFER, H., and WEISS, L., *Lieb. Ann.*, **320**, 237 (1901); WÖHLER, F., *Z. Elektrochem.*, **11**, 612 (1905); ARNDT, K., and WILLNER, K., *Ber.*, **40**, 3025 (1907); OETTEL, F., Dissertation, Dresden (1908); KAILAN, A., *Z. anorg. Chem.*, **68**, 141 (1910); particularly FRARY, F. C., and BADGER, W. L., *Trans. Am. Electrochem. Soc.*, **16**, 185 (1909); OESTERHELD, G., and BRUNNER, H., *Z. Elektrochem.*, **22**, 38 (1916); ARNDT, K., and PROBST, H., *ibid.*, **29**, 323 (1923); TAYLOR, C. S., *Trans. Am. Electrochem. Soc.*, **47**, 301 (1925).

[8] LORENZ, R., *Z. anorg. Chem.*, **10**, 78 (1895).

The silver is deposited first, then the lead, and finally the zinc.

Electrolysis. Lorenz,[9] in his investigations of a large number of fused electrolytes, found that the behavior of these differs markedly in a number of respects from the behavior of dilute aqueous solutions. The equilibria between fused salts and molten metals were studied by Lorenz and Fraenkel.[10] They have recorded the effect of diluents to the salt phase and to the metal phase in various reactions. Results obtained depend greatly upon whether or not the diluent be a strictly indifferent salt or metal. The results are given in detail and the most probable explanation presented. The law of mass action, which holds rigidly for dilute solutions and ideal gases, does not apply to fused electrolytes. However, Lorenz developed a modified equation for the law of mass action which does apply to condensed systems.

Aten, Hertog, and Westenberg[11] investigated the electrolysis of fused electrolytes in which the resulting metal was deposited in the solid and not the molten form. Experiments were confined largely to silver and copper salts, since the melting points of silver and copper are noticeably higher than the melting point of their halide salts. Irregularities in the distribution of the deposit resulted from differences in the temperature of the cathode plate, the tendency being for the metal to redissolve from the hotter portions of the cathode and to build up on the colder sections. On silver cathodes with an original crystalline surface, the deposited crystals grew as a continuation of the grains in the plate. Polarization voltage was low in all the electrolytes and decreased with rising temperature of the bath. Although there was a variation of the grain size of the deposited silver, copper, or nickel, depending upon the temperature and composition of the bath, the great differences which exist between the structure of these metals when electrodeposited from aqueous solutions do not exist at the higher temperatures of the fused baths. A crystalline deposit was obtained in experiments with fused manganese and iron salts.

[9] LORENZ, *op. cit.*

[10] LORENZ, R., and FRAENKEL, W., *Trans. Am. Electrochem. Soc.*, **47**, 249 (1925).

[11] ATEN, A. H. W., HERTOG, H. J., and WESTENBERG, L., *Trans. Am. Electrochem. Soc.*, **47**, 265 (1925).

The first record of a fused electrolyte was given by Sir Humphry Davy in 1802.[12] Since his time the electrolysis of fused salts has been applied as a method for either the discovery or the commercial preparation of many metals, among the most important of which are Ca, Sr, Ba, Na, K, Li, Cs, Rb, Mg, Al, Be, Ce, Ta, Ra, Tl, Ti, U, V, as well as many valuable alloys.

The metals produced in tonnage amounts by fused salt electrolysis are aluminum, magnesium, and sodium, while beryllium and its alloys, calcium, cerium, columbium, lithium, lead alloys, and zirconium are manufactured ᵇy related processes but only in relatively small quantities. The process for their preparation will be discussed in the order mentioned above.

Aluminum is made in a cell with an electrolyte whose melting point is higher and whose specific gravity is lower than that of aluminum so that the metal sinks to the bottom of the cell and is drawn off there. Magnesium is lighter than its electrolyte and is taken off at the top. Sodium is similar to magnesium, but its specific gravity is so much lower than its electrolyte that it can be elevated out of the cell by displacement. Lithium is similar to sodium. Calcium cells are special in that the current density required is so high that only a "contact" of the cathode is needed, and metal freezes around the cathode. Beryllium has a higher melting point and density as compared to the electrolyte so that it sinks to the bottom of the cell as a solid nonagglomerated metal and cannot be tapped from the furnace. It is separated by dissolving the frozen electrolyte away from the metal. Cell designs and operation are dependent largely on the specific characteristic of each metal and its electrolyte, so that the cell designs show marked variation.

ALUMINUM

In the manufacture of aluminum there are two main stages. The first embraces the production of pure Al_2O_3 (alumina) from some aluminous mineral, usually bauxite, and the second is the reduction of this Al_2O_3 to the metal in a bath of fused cryolite. The reason for these two stages is that impurities in the raw materials must be removed. Bauxite, for example, usually contains alumina, iron oxides, silica, and titania. If it be directly

[12] DAVY, SIR HUMPHRY, *J. Royal Inst.*, **53**, (1802); *Phil. Trans.*, **98**, 1 (1808).

electrolyzed or dissolved, a considerable proportion of these impurities will appear in the aluminum or salts. Hitherto it has proved more practicable to make the pure alumina and then the pure metal or salts than to refine an impure metal or purify crude salts.

Because of the commercial importance of aluminum and its salts, a large number of experimenters have proposed processes for making pure alumina and pure aluminum compounds from various aluminous minerals such as cryolite, bauxite, clays and kaolins, labradorite, alunite, leucite, shales, feldspar, and others. The mineral most commonly worked for alumina is bauxite, mainly refined by the Bayer process.

Alumina Production. The technical process and carefully balanced reactions necessary to refine bauxite to alumina are peculiar to this metal. While necessary for the ultimate production of high-purity aluminum, they constitute a heavy charge on every ton of metal produced. Aluminum will probably never be smelted from its ores like iron. It is not expected that it will be electrolytically refined from an aqueous solution like copper. It is believed that the refining of aluminous ores will continue to involve chemical processes of some delicacy, calling for appreciable investment in plant and significant amounts for fuel, labor, and reagents. This is true whether the raw material be the conventional grades of red bauxite, alunite, leucite, kaolin, labradorite, or other material.

The more important processes used for production of high-purity alumina are (1) Bayer, (2) Hall, (3) Pedersen, and (4) Haglund. These will be briefly discussed in their chemical engineering and economic aspects.

1. *Bayer Process.* In this process a high grade of bauxite is a necessity. A high grade of alumina is usually produced. Composition of the ore may be as follows: Al_2O_3 60 to 55 per cent, Fe_2O_3 25 to 20 per cent, TiO_2 2 to 3 per cent, SiO_2 1 to 3 per cent, H_2O and organic impurities 12 to 15 per cent. The ore is crushed, ground in a ball mill to 70 mesh, mixed with a strong soda liquor and digested with steam at 60-lb pressure to dissolve the Al_2O_3. Digestion is carried on in autoclaves at 150°C for 8 hr. The solution is blown into tanks and diluted to a density of about 1.20. It is then filter-pressed, the iron oxide remaining in the residue with most of the TiO_2. From the clear solution of $Na_2Al_2O_4$,

the alumina can be precipitated in large tanks or decomposers by slow agitation and the addition of a small proportion of reserve aluminum hydrate. The precipitate is then thickened, washed, dried, and calcined at 1100°C in a rotary kiln. In a modification of the Bayer method, the ore is ground, mixed with the appropriate quantity of Na_2CO_3, and roasted at about 1000°C, when $Na_2Al_2O_4$ will be formed by decomposition of the carbonate. The solid mass after cooling is leached with distilled water and the clear liquor treated in decomposers to precipitate alumina, as above.

The Bayer process is not easy to operate and control. The filtration problems alone are perhaps as difficult as those in any other technical process. Both in Europe and in America the Bayer process has long been in commercial operation. American practice also favors thickeners in place of filter presses for the separations employed. A good and invariable composition of bauxite is needed. Low silica is essential, 3 per cent being the upper limit. The objection to silica lies in its rendering a portion of the alumina insoluble, thus hindering the recovery from a given ore. A good, pure alumina for use in the reduction furnaces contains less than 0.01 per cent FeO.

The chemical engineering flow sheet of the method of alumina production is shown in Fig. 166. Mantell[13] reviewed the refining methods in use and proposed for aluminous ores.

2. *Hall Process.* At the beginning of the aluminum industry in the United States, Charles M. Hall devised an electrical method for the refining of bauxite. Bauxite of graded composition is ground to a granular form and mixed intimately with an appropriate weight of coal similarly ground. The mixture is then sintered at about 1000°C, cooled, and a further quantity of coke introduced for the purpose of reducing the impurities. The mixture is then smelted in a furnace using electrodes of the Söderberg type at about 2500°C. Ferrosilicon and ferrotitanium sink to the bottom of the bath and are tapped off. Pure alumina is blown off by steam and air pressure from the top of the furnace into an iron-lined chamber where it is precipitated in flocculent particles similar to popcorn. Contamination by carbides is likely to be the chief difficulty. The alumina after cooling is leached with hot water and dilute H_2SO_4 to remove traces of

[13] MANTELL, C. L., *Chem. & Met. Eng.*, **35, 746** (1928).

Bauxite (55-60% Al₂O₃)	2600 lb	
NaOH make-up (76%)	80 lb	
Water	6300 gal	

$$Bauxite\ (55\text{-}60\%\ Al_2O_3)\quad 2600\ lb$$
$$NaOH\ make\text{-}up\ (76\%)\quad 80\ lb$$
$$Water\quad 6300\ gal$$

Steam	15,000 lb	
Electricity	180 kwhr	Per ton dry hydrate, $Al_2O_3 \cdot 3H_2O$
Direct labor	3.8 man hr	
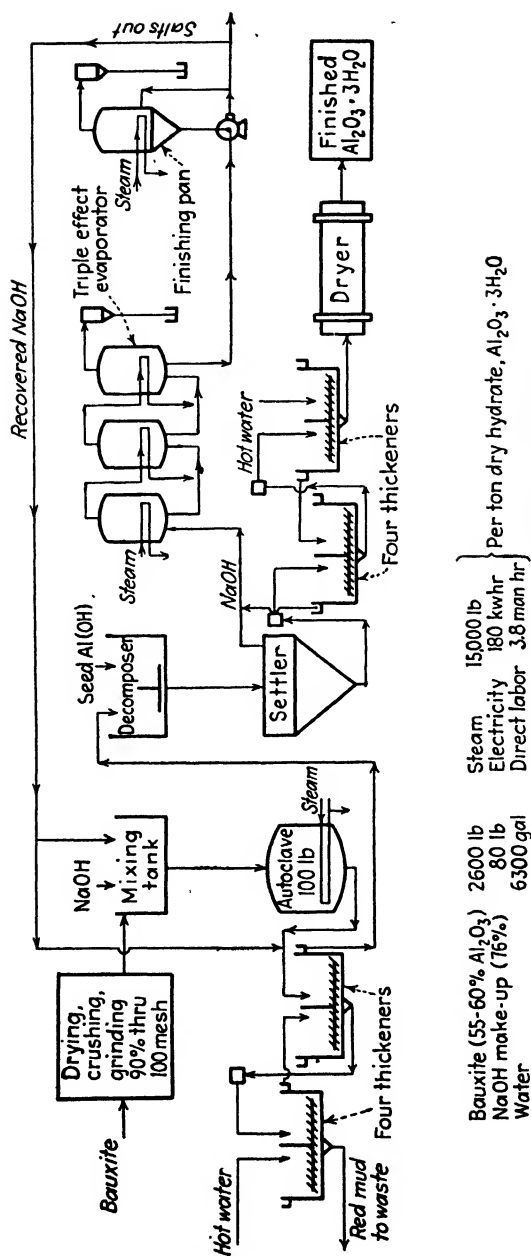
Fig. 166.　Alumina (Bayer process).　(*Chemical Engineering.*)

titanium oxide.   The solids are filtered in such a way as not to crush or deform the grains.   This process was commercially operated at Badin, N.C., and Arvida, Que.   The resulting alumina is in the form of solid bubbles.   It has only one-third the density of amorphous Bayer alumina.   This is advantageous as a charge for the reduction furnaces.   As outlined, the improved Hall process constitutes a method of treating bauxite of lower grades than are available for the Bayer process.   In the latter, iron and silica are separately removed; in Hall's method, they are removed in combination 'by simultaneous reduction. Although accurate balance mus' be maintained in the charge, a silica content greater than 3 per cent is no longer embarrassing.

3. *Pedersen Process.*[14]   The Pedersen process is in operation at Høyanger in Norway at the works of the Norsk Aluminum Company with a capacity of 16,000 tons of alumina per annum using bauxite with 4 to 5 per cent SiO_2, and at Sundsvall in Sweden the works of the Svenska Aluminiumkompaniet with a capacity of 8,000 tons per annum using andalusite.   There is no bauxite in Scandinavia, and during the Second World War andalusite ($Al_2O_3 \cdot SiO_2$) from Boliden in the north of Sweden was used.   Bauxite is imported from Europe.

The Pedersen process can use low-grade aluminous ores.   An electric smelting furnace is used.   The charge consists of iron ore, limestone, and bauxite in the required proportions, although the iron ore is usually omitted.   Coke must also be included in the charge.   The chemical reactions in the furnace are as follows: The Fe_2O_3 content in the charge, if there is any such content of importance, is reduced to pig iron containing about 0.5 per cent Si and about the same percentage of Ti, but the main part of the SiO_2 and the TiO_2 in the charge is slagged off as calcium silicate and calcium titanate together with the alumina.   The latter is united with the CaO in the charge to a mixture of calcium aluminates, and this reaction is the main chemical reaction in the smelting part of the Pedersen process.   Three-phase direct-arc furnaces with Söderberg electrodes are used.

The slag is tapped off, cooled, crushed, and leached with a hot solution of dilute Na_2CO_3 containing 10 per cent of free caustic. The leaching solution contains about 2 per cent Na_2CO_3, and

[14] Private communication from Lars Barr, Svenska Aluminiumkompaniet, Sundsvall, Sweden.

about 10 per cent of the Na_2CO_3 content is present as free caustic. The main reaction in the extraction part is that the calcium aluminates when introduced into the Na_2CO_3 lye precipitate the less soluble $CaCO_3$. The reaction is

$$CaO \cdot Al_2O_3 + 4H_2O + CO_3^{--} = CaCO_3 + 2Al(OH)_4^-$$
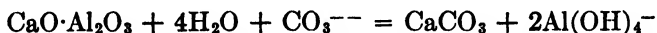
The SiO_2 and TiO_2 compounds in the slag do not ordinarily get into solution, if the extraction is carried out under careful control.

After the extraction, the slime containing $CaCO_3$ is pumped to thickeners for the separation of slime and solution, and the overflow from them, the sodium aluminate solution, after filtration is pumped to Pachuca tanks where CO_2 (combustion gases from the calcining of the $Al(OH)_3$) is blown into the solution causing the reaction

$$CO_2 + 2Al(OH)_4^- = CO_3^{--} + 2Al(OH)_3 + H_2O$$

The $Al(OH)_3$ is filtered off and calcined to alumina, and the regenerated Na_2CO_3 solution is returned to the extraction tanks.

The flow sheet is shown in Fig. 167. The method permits the use of bauxites of high iron and silica content which are not economically treatable by the Bayer method.

4. *Haglund Process.* Because of the high-purity ore required by the Bayer process and the exact balance which must be maintained between the reacting agents, attempts have been made to substitute methods for dealing with lower grade minerals of a wider range of composition. The method of T. R. Haglund, introduced several years ago in Sweden, was developed experimentally in Germany and is operating commercially in Italy. Aluminous ore, usually bauxite, is crushed and mixed with a due proportion of anthracite and pyrites or other metallic sulfides. The proportions will obviously depend upon the iron, silicon, and titanium impurities in the ore. On fusing the mass in a smothered-arc or resistance furnace, the iron, silicon, and titanium are reduced and tapped off. The slag containing the aluminum is cooled, when a part of it will crystallize out as alumina, the remainder being Al_2S_3. The latter amounts to about 20 per cent of the total slag. This is sufficient to hold the alumina in solution at the furnace temperature of 1100°C.
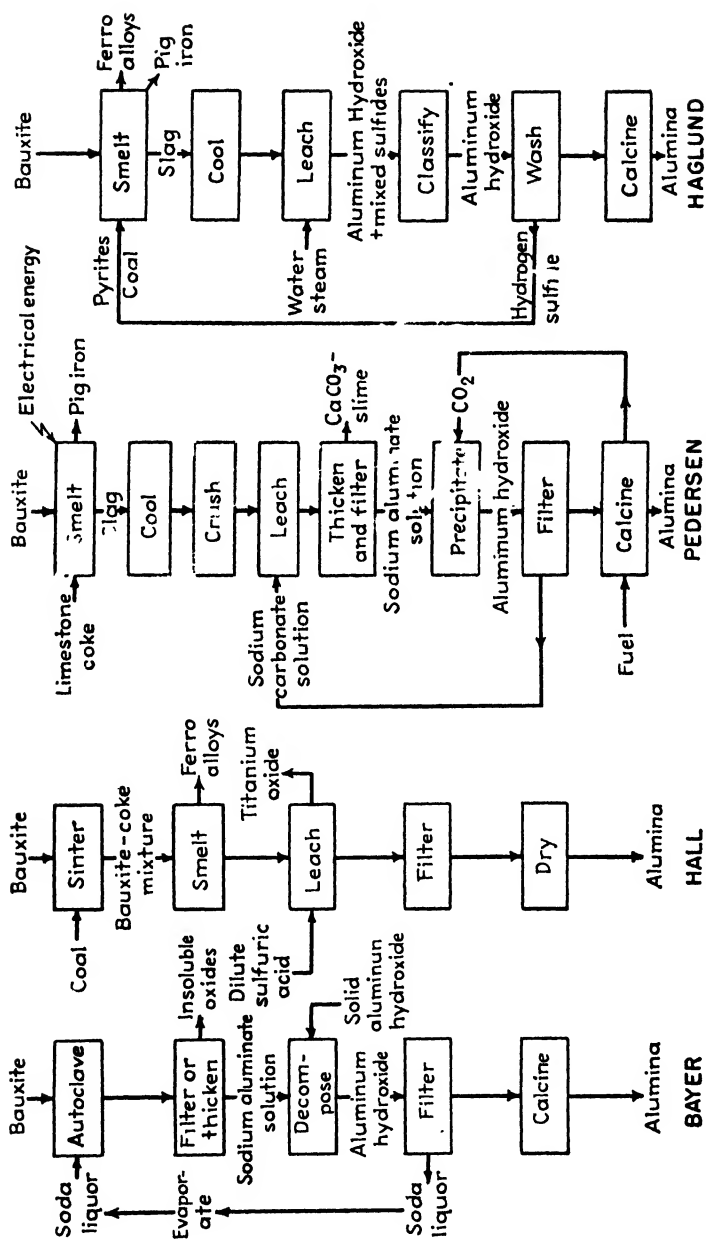
Fig. 167.   Flow sheets of the Bayer, Hall, Pedersen, and Haglund processes.

The main furnace reaction is, approximately,

$$Al_2O_3 + 3C + 3FeS = Al_2S_3 + 3CO + 3Fe$$
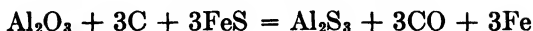
The outstanding feature of the process is the utilization of the fused sulfide as a flux or solvent for the aluminum and as a means of reducing its melting temperature. The mixed slag is cooled, crushed, and leached with water and steam:

$$Al_2S_3 + 6H_2O = 2Al(OH)_3 + 3H_2S$$
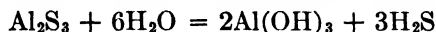
After leaching, the residue contains not only the aluminum hydrate but also mixed oxides and sulfides of iron, titanium, etc. The material is treated by classifying and concentrating, when $Al(OH)_3$ containing a percentage of crystalline alumina is removed. The crystalline alumina is washed with warm H_2SO_4 and dried. The hydroxide is then dried and calcined in the usual way. The H_2S is condensed and regenerated for sulfurizing a further furnace charge.

In practical operation, low-grade materials as carboniferous clay, coal dross, and the like are charged. Pig iron is one of the important by-products of the process. The market for this and the ferroalloys will have a bearing on the field for Haglund methods.

Primarily Haglund's method applies to bauxite having a silica content too high for treatment by the Bayer process, particularly when the alumina content is correspondingly low. In the diagram it should be noted that the preliminary sulfurization is necessary only where the iron content in the bauxite is high. By this treatment the charge of sulfide can be reduced, and the process becomes more nearly regenerative. Where this is not done, the H_2S is condensed and the sulfur regained in a Claus furnace.

Electrolysis of Alumina. The world's production of aluminum is obtained by the electrolysis of a solution of alumina in fused cryolite ($AlF_3 \cdot 3NaF$). The process is based on the patents (1883–1889) of Hall in the United States and Héroult in France.

Fundamentally, aluminum is produced by the electrolysis of alumina dissolved in a bath of aluminum fluoride and the fluoride of one or more metals more electropositive than aluminum, such as sodium, potassium, or calcium. Cryolite melts at about 1000°C and at temperatures slightly above its melting point is

able to dissolve as much as 10 to 20 per cent of its weight of alumina with resultant decrease in its melting point, as shown in the diagram of the freezing points in the cryolite-alumina system in Fig. 168. The freezing points of the aluminum-fluoride sodium-fluoride system are given in Fig. 169. If a direct current be passed through the solution of alumina in cryolite or alumina in cryolite plus other fluorides, the alumina is decomposed, the aluminum being deposited at the cathode in a molten condition
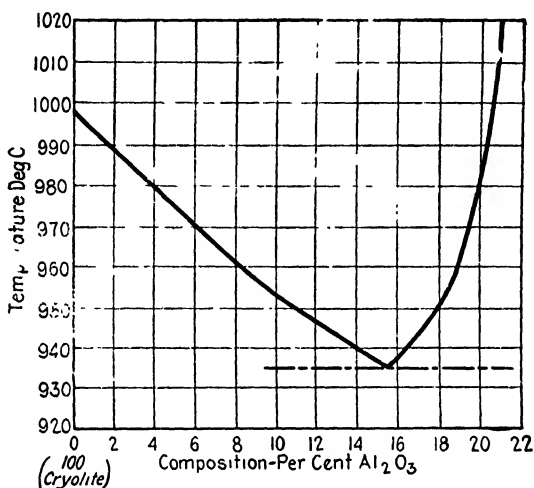
FIG. 168. Freezing points in the cryolite-alumina system.

(melting point about 660°C) and oxygen at the anode, which is carbon, with which the oxygen reacts to form the probable primary product of CO_2. This is believed to be subsequently reduced to CO by the hot carbon. The thermal effect of the oxidation of the carbon anodes is to reduce the amount of electrical energy required to maintain the bath in a fused state. The bath itself is not appreciably decomposed by the current.

At the operating temperature the fused cryolite, or modified bath, and molten aluminum are very reactive and destructive of containers. Hall solved the problem by the use of an iron crucible or box lined with carbon. To date no better materials of construction have been found.

Reduction Cell. The reduction cell or "pot" is a strong steel box, usually rectangular in shape, provided with a carbon lining 6 to 10 in. or more in thickness. Figure 170 shows the essentials
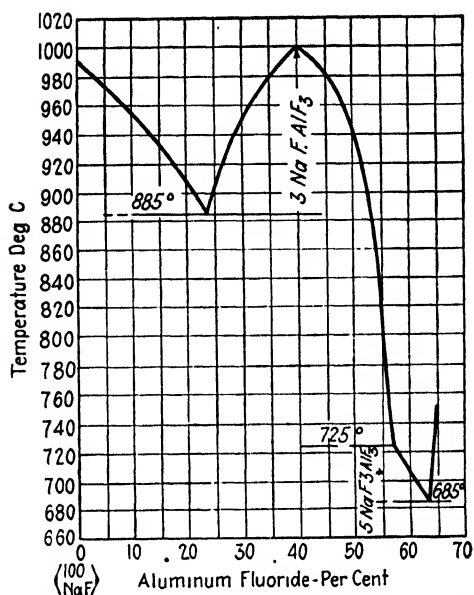
FIG. 169.   Freezing points in the sodium-fluoride aluminum-fluoride system.
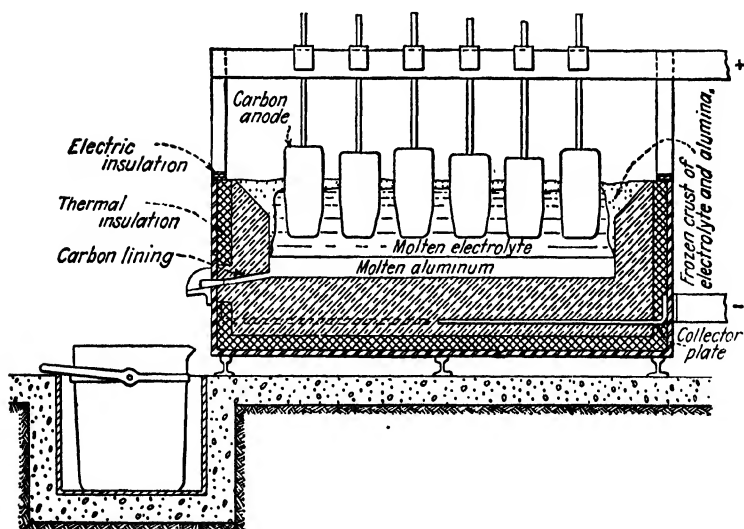
FIG. 170.   Aluminum cell.

of such a cell. The steel plate used for the pot is 1 to 2 in. thick and makes contact either directly or through collector plates with the carbon lining. The steel shell is thus employed to carry current to the carbon cathode. In some cases insulating material is used between the carbon lining and the shell for the saving of heat, with presumable reduction of power needed to maintain the proper temperature. There appears, however, to be considerable difference of opinion as to the real advantages of thermal insulation when all factors are taken into account. In marked contrast to the electrolysis of magnesium com,ounds, external or auxiliary heating is unnecessary and impra׳׳ al.

External and internal dimensions of the cell and lining vary considerably with current capacity. The smallest cells are 8,000 amp, but the average is between 20,000 and 28,000 amp, with 40,000- to 50,000-amp cells as American and British standards. Generally the more current that can be used in a cell, the lower will b, the producing cost of a pound of aluminum. Aluminum production is approximately proportional to the current, while it takes just about as much labor to run a small cell as a large one. The limit of current capacity is set by increase in difficulties involved in changing anodes, breaking the frozen top crust, and operating the larger cells. For multiple electrode pots, the practical limit is almost reached at 40,000 amp, but commercial cells are operating at 50,000-amp load.

In practice, the current densities, cell voltages, and thermal insulation are so adjusted as to maintain the cell at the proper working temperature. Commercial cells have operated with currents of from 8,000 to 50,000 amp, voltages from about 4.5 to 7, and current efficiencies of 80 to 90 per cent. A number of such cells have been described in the reports of inspections of the German aluminum plants[15] and the various monographs on aluminum.[16] A line of 50,000-amp cells is shown in Fig. 171.

---

[15] von Zeerleder, A., *Aluminium*, **18**, 163 (1936); Lux, L., *Aluminium*, **21**, 362 (1939); Anon., *Aluminium*, **22**, 613 (1940); Hunter, R. M., *CIOS Rept.* XXV-17; Hall, H. H., and Kemp, J. T., *CIOS Rept.* XXXII-59; Haenni, P. M., and Peake, T. J., *BIOS Final Rept.* 279; Black, J. C., Akers, J. R., and Sherwin, R. S., *FIAT Final Rept.* 524; Cunningham, A., *FIAT Final Rept.* 731; Frary, F. C., and Rice, A. J., *FIAT Final Rept.* 933.

[16] Engel, N. H., Gregory, H. E., and Mossé, R., "Aluminum, an Industrial Marketing Appraisal," pp. 7–12, Richard D. Irwin, Inc., Chicago, 1944;

Cathodes. The carbon cathode must have adequate strength, have good electrical conductivity, and be so fashioned that it will remain in place and carry the current to the metallic aluminum. Overheating and local stresses cause it to crack and disintegrate. Broken pieces of lining may then float in the bath and cause partial short circuits between the anodes and the metal. Breaks

FIG. 171. A line of 50,000-amp cells for the production of aluminum. (*Aluminum Company of America.*)

in the lining may permit the molten aluminum metal to attack the steel shell or collector box, with resultant solution of the iron by the aluminum. Such a pot "makes steel" in the language of the operator. It must be removed from the line for repair. The carbon lining is somewhat porous and absorbs nearly its own weight of the fused electrolyte. When cells are removed from the circuit for repair, the old linings are broken out. In most modern practice the fused electrolyte is recovered by burning off the carbonaceous material in multihearth furnaces of the roasting type.

EDWARDS, J. D., FRARY, F. C., and JEFFRIES, ZAY, "The Aluminum Industry," Vol. I, pp. 301–307, McGraw-Hill Book Company, Inc., New York, 1930.

Two types of cathode linings are employed. One is made by ramming a hot mixture of pulverized coke with tar and pitch binders into the steel shell, using a suitable cast-iron form to give the cavity the desired shape. The entire pot is baked in a furnace at about 600 to 800°C. In the second method, preformed and prebaked carbon blocks are used to build up the lining, the blocks being cemented together with a mixture of tar, pitch, and ground coke. In practice, cells may last from as short a time as 1 week when they are poorly made, to as long as 3 years without repair or replacement.

Anodes. The anodes are carbon made from petroleum coke.[17] Their manufacture is discussed in connection with materials of construction.

The anodes are hung from two or more copper or aluminum busbars supported above the cell. They depend from rods or bars of aluminum, copper, or iron which connect onto the busbars by adjustable clamps and carry current to the anodes. Proper adjustment of the anodes for equalization of the current passing through them is one of the most important factors in the operation of the pot. Anodes set too low may allow projecting points to touch the metal layer in the bottom of the cell, thus short-circuiting it; anodes set too high may, because of the resistance of the thicker layer of electrolyte between them and the cathode, fail to carry their proper share of the current.

To reduce to a minimum the impurities in the aluminum produced, it is obviously necessary that the carbon anodes have a minimum ash content.[18] In manufacturing them, it is therefore necessary to use calcined petroleum coke or pitch coke instead of foundry coke. The prebaked carbon anodes, which generally have been employed until recently throughout the aluminum industry, may be either round or rectangular in cross section and have varied in size from 4 in. (102 mm) diameter round rods to a rectangular cross section of roughly 15 by 50 in. (380 by 1,270 mm). They are supported by suitable copper or aluminum hangers clamped to anode busbars over the cell, and arranged so as to distribute the current uniformly over the cross section of

---

[17] MANTELL, C. L., "Industrial Carbon," 2d ed., D. Van Nostrand Company, Inc., New York, 1946.

[18] The consumption of carbon electrodes is about 60 to 65 per cent of the weight of aluminum produced.

tbe molten bath and hence over the surface of the molten alumi-
num cathode on the bottom of the cell.   Cathode current densi-
ties vary considerably in different designs and different sizes of
cells but are generally between 300 and 600 amp per sq ft (0.32
to 0.65 amp per cm^2).   Actual anode current densities are more
difficult to estimate because the sides of the anodes are active as
well as the bottoms, but the longer current path involved pro-
duces a lower current density on the sides than on the bottoms
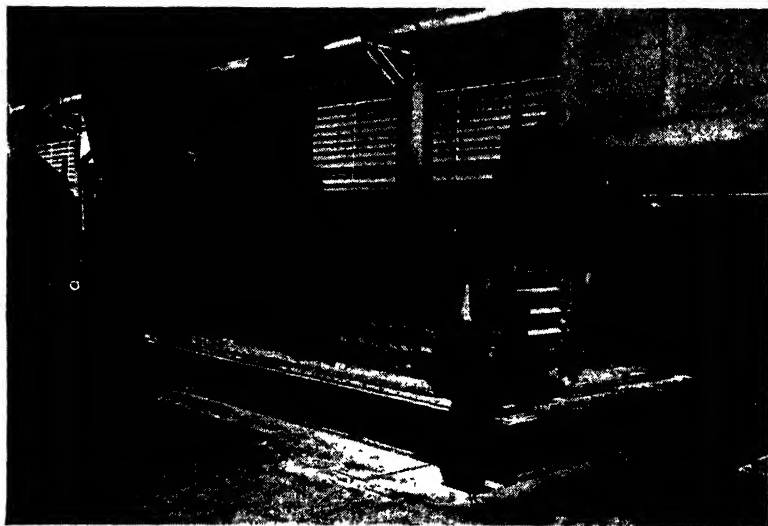
Fig. 172.   Aluminum cell with Söderberg electrodes in a plant of the Olin Cor-
poration, Tacoma, Wash.   (*Mining and Metallurgy.*)

of an anode.   It is customary to neglect the side areas and figure
the density on the basis of the bottom area only.   Currents of
5 to 7 amp per sq in. (0.77 to 1.1 amp per cm^2) have been reported
on this basis and are probably representative.   An aluminum
cell with Söderberg electrodes is shown in Fig. 172.

Cell Operation.   During working, the cell contains a layer of
molten aluminum, varying in thickness from a fraction of an inch
up to 4 or 5 in.   Molten aluminum (sp gr 2.29 at 1000°) is
heavier than molten cryolite (sp gr 2.095 at 1000°).   Unless
the contents of the cell be very violently agitated, the metal will
remain at the bottom.   Solid alumina, which is periodically
added to the bath, is more dense than cryolite, but the solution
of alumina in liquid cryolite is lighter at the same temperature

than cryolite without dissolved alumina. Calcium fluoride when added as a bath addition agent increases the density of the liquid cryolite. In the pot, then, there is a layer of 6 to 12 in. of molten electrolyte. This is essentially a solution of alumina, usually 2 to 5 per cent, in molten cryolite which may contain other fluorides either purposely added or resulting from the ash of the electrodes. Above the molten electrolyte is a crust of frozen electrolyte mixed with aluminum oxide. The anodes project through this crust so that their lower ends are 2 to 4 in. above the upper surface of the layer of molten aluminum at the bottom of the cell.

In operation, the bubbles of gas even off at the anodes, as well as the magnetic field effect produced by the large currents passing through the anode buses, the cell walls, and the lining, continuously agitate the electrolyte. The aluminum oxide added to the cell from time to time is considerably heavier than either the molten electrolyte or the molten metal. Were there no agitation, the alumina would sink to the bottom of the cell and accumulate under the metal layer. This would prevent the electrolyte from dissolving it readily, and would cause increased resistance and overheating at the contact between the metal and the carbon lining. If the alumina be fine enough, even though of the fused variety (sp gr 4), it is maintained in suspension, long enough to be dissolved, by the agitation of the electrolyte. Edwards[19] states that the actual time required for 200-mesh alumina to dissolve completely in fused cryolite (2 g alumina in 150 g cryolite) has been found by experiment to vary between $1\frac{1}{2}$ and 9 min, depending on the temperature, degree of saturation of electrolyte, and the character of the alumina, whether porous as produced in the Bayer process, or compact as made by grinding up electrically fused alumina.

At 1000°C the density of molten cryolite is just under 2.10, while that of molten aluminum is approximately 2.284.[20] Since the fluorides of calcium, barium, and strontium markedly increase the specific gravity of cryolite, it is evident that the amounts of these substances present must be carefully kept below a point at which the bath would become so dense that the agitation produced in it during normal operation would cause aluminum globules to float and be carried to the anode where they would be

[19] EDWARDS, FRARY, and JEFFRIES, *op. cit.*

[20] EDWARDS, J. D., and MOORMAN, T. A., *Chem. & Met. Eng.*, **24**, 61 (1921).

oxidized. In practice, barium and strontium are present only in traces, and the amount of calcium fluoride is kept below about 15 per cent so as to leave an adequate margin of safety. It is evident that this puts a stringent limitation on the CaO content of the alumina; in practice this should not exceed about 0.04 per cent. Some new cryolite is formed in the bath by the regular addition of aluminum fluoride to neutralize the soda (about 0.6 per cent Na_2O) contained in the alumina employed and there is some mechanical loss of bath due to spillage, absorption in the lining, electrode butts, and carbon raked out of the cell and discarded, etc. In general, the dilution by new cryolite formed or added almost compensates for the calcium fluoride formed from the lime in the alumina and electrode ash. The total consumption of bath materials is reported to be between 4 and 7 lb per 100 lb of aluminum.[21]

As the electrolysis continues, alumina is consumed in direct proportion to the metal production. As the alumina concentration in the electrolyte is reduced, a point is finally reached where the anode effect occurs. The actual concentration of alumina probably depends upon the temperature, the composition of the electrolyte, and the anode current density, but is generally likely to be about 2 per cent. The occurrence of the anode effect is the signal for the addition of more alumina. The attendant does this by breaking the frozen layer, on top of which he has previously distributed a layer of alumina. The addition of the alumina, as well as a vigorous stirring of the electrolyte, causes the anode effect to disappear, after which the electrolysis continues its normal course for several hours, when addition is again needed.

The nature and cause of the anode effect have received considerable attention from investigators.[22] It manifests itself in a sudden rise in the voltage across the cell, from 6 to 7 volts up to 30 or even 60 volts. As a means of detecting this change, an incandescent lamp is connected across the terminals of the cell and mounted near it. When the anode effect occurs, the lamp, which had been glowing dimly, flashes up and gives a bright light. This attracts the attendant and shows him that it is time to "work" the cell. Careful examination of the cell when the

[21] ENGEL, GREGORY, and MOSSÉ, *op. cit.*, p. 212.

[22] ARNDT, K., and PROBST, H., *Z. Elektrochem.*, **29**, 323 (1923); TAYLOR, C. S., *Trans. Am. Electrochem. Soc.*, **47**, 301–316 (1925).

anode effect occurs shows that the electrolyte no longer "wets" the anodes, as water wets glass, but there is a continuous gaseous envelope covering the whole of the surface of contact between each anode and the electrolyte, and the current is passing through this envelope as a multitude of tiny sparks or arcs.   The whole of the voltage increase is localized in this gaseous envelope, and the anode surface and the gas are therefore highly heated.   Oxygen resulting from alumina decomposition is constantly reacting with the anode material.   This gives a continuously cleaned anode surface.   Impurities in the carbon anode are thought to produce a condition of the anode called "dusting,' in which the surface becomes covered with a layer of dust.   An anode so covered favors the anode effect.   It is also believed that aluminum fluoride separates from fused cryolite low in alumina, and that this material produces a turbidity of the bath and deposits on the anode as a nonconducting layer.   Once separated, aluminum fluoride dissolves again slowly.   All these factors—the dusting of the anode, the layer of aluminum fluoride on it, and the turbidity of the bath—may be regarded as causes of the anode effect.   By disturbing the intimate contact between the anode and the melt they provide a foothold for the gas film which produces the anode effect.   Chemical analysis shows that during the anode effect the gas evolved is pure CO, whereas at other times it contains from 50 to 90 per cent CO_2.   Thus, since a given amount of oxygen liberated at the anode will produce twice as large a volume of CO as of CO_2, and since the volume of a gas is directly proportional to its absolute temperature, the film of gas represents a very abnormal volume evolved at each anode.   Likewise, it represents nearly double the normal carbon consumption and five or ten times the normal heat evolution and power consumption, so every effort is made to "kill the light" and restore normal conditions as rapidly as possible.

The theoretical emf for the dissociation of alumina in the Hall-Heroult process is 2.8 volts, but actually the requirement becomes two to three times this value.   The resistance of the bath, contact drops at joints and connections, and slight losses throughout the circuit necessitate a greater difference in potential, since each cell takes a large current at low voltage, a number of cells are arranged in a line in series.   An arrangement is thus effected causing a summation of the voltages so that

the line may be connected to a "standard" generator voltage. This is a much more economical arrangement than the employment of low-voltage motor-generator sets.   The line voltage may be anything between 200 and 600 volts, depending on power conditions, design of plant, busbar arrangement, and other factors.   A line may contain 30 to 100 pots in series.   Because the line current passes through all the cells in series, any happening such as the appearance of the anode effect in one cell changes electrical conditions slightly in all the cells, and also affects the total load on the line.   The greater the number of cells in the line, the less will be the disturbing effect of any change in one cell.   Cell voltages, including busbar and cable IR drops, may vary between 5 and 7 volts, depending upon the circuit design, the age of the cells, the state and type of the electrolyte, the anode-cathode distance, and other factors.   These same factors enter into the power requirements per pound of aluminum with the addition of the human operating element and the resultant care given to the cells.   The power requirements for aluminum are 10 to 12 kwhr per lb, although in some plants this figure is as low as 9.5 kwhr per lb.   Anode consumption varies, depending upon the quality of the anodes, size, shape, and skill with which the cells are operated.   From 0.6 to 0.8 lb of carbon per pound of aluminum is considered satisfactory for an efficient plant, although the figure at times may become as great as 1 lb of anode per pound of aluminum.   The alumina requirements are of the order of 2 lb of alumina for 1 of aluminum.

When a sufficient amount of metal has accumulated in the bottom of the cell, it must be removed by either tapping or ladling.   This may be done every day, every second day or third day, depending upon the design of the cell, the ideas of the management, and local conditions.   When the metal is to be tapped out, the tap hole is opened by driving into it a sharp steel tapping pin.   When enough metal has been removed, it is closed. From the tapping ladle, the metal is transferred into a larger pouring ladle.   The metal from several cells is accumulated in this pouring ladle, then skimmed with a perforated skimmer and poured into molds of about 50-lb capacity each.   When the metal is to be ladled out, an anode is removed and a heavy cast-iron cylinder is set into the cell in its place.   As the molten electrolyte is now ladled out of the cylinder, the metal rises to

take its place. When it appears, it is ladled off into molds. Each cast must be analyzed and graded, so that casts may be chosen and mixed in the remelting furnace to produce the grade desired by the customer. Another common practice is to pour the molten aluminum from the tapping or pouring ladles into a "holding furnace." In this way the metal from many cells is blended, and finished ingots may be cast from it. Practically all commercial aluminum is remelted or heated in holding furnaces to ensure uniformity of compositions and the removal of nonmetallic impurities.

The electrolytic cell can be started by pouring a suitable amount of molten electrolyte into it, adjusting the anodes, and passing current. Usually, however, molten electrolyte in sufficient quantity is not available, and the electrolyte must be fused in place. To do this, the anodes are grounded on the carbon bottom of the cell, and some solid electrolyte is shoveled in around them. On passage of the current, sufficient heat develops at the point of contact of anode with cathode to fuse the surrounding electrolyte gradually. When a molten layer of sufficient depth has been formed, the anodes are raised, electrolysis commenced, and more electrolyte added until the cell is filled to the proper height.

When a cell is to be taken out of service, the electrolyte can be tapped out or, as is more usual, the anodes removed and the cell contents allowed to solidify. It is highly important that the power supply be continuous, for if it be discontinued for many hours, the cell contents will solidify. If power fail, it is sometimes possible to ground the anodes on the bottom of each cell and later, after the cell contents are frozen, to increase the current through the cells cautiously until the contents are again molten. The process is hazardous, however, because the starting current is irregularly distributed and results in the burning off of anode supports and the expulsion of molten electrolyte from time to time. After a cell is frozen, the contents can be dug out, part of the electrolyte salvaged, and the cell relined for use.

Energy Efficiency. The efficiency of the reduction process is affected by many factors such as the design of the cell, the operating conditions of current and voltage, but most important of all, the skill and constancy of attention of the workman caring for the cell. Theoretically, 1,000 amp-hr at 100 per cent

efficiency will produce 0.74 lb of metal per hour. In practice, the current efficiency is between 75 and 90 per cent. It is reduced by short circuits resulting from improper adjustment of the anodes, current leakages through the crust, and reoxidation of reduced metal. Electrode adjustment is a function of labor efficiency. Metal fog or mist, so common to fused salt electrolysis, may result from extremely small particles of metallic aluminum suspended in the electrolyte. The metal mist is being constantly brought into contact with the anode surfaces as a result of the agitation owing to electromagnetic forces. At the anodes, the metal in the form of fog may be reoxidized to alumina. The loss of metal by reoxidation can be reduced by increasing the space between the bottom of the anode and the top of the molten metal. This, however, increases cell resistance and power consumption, so that loss by reoxidation must be balanced against increased power requirements.

Thermodynamic calculations indicate values of 0.09 to 2.0 volts for the decomposition of alumina, depending upon the fundamental assumptions made. An experimental determination of the decomposition voltage of alumina in cryolite is a difficult one. Estimates made from the current-voltage curves over a wide range of currents indicate potentials of 1.7 volts, while the operating voltage is between 5 and 7.

In addition to that required for the decomposition of alumina, power is necessary for heating the electrolyte and maintaining its molten condition. In general, all power greater than that required to decompose the alumina must be dissipated as heat. Thermal radiation losses can be decreased by suitable insulation, but the practical advantage of this has been questioned. In the United States at least, such insulation is not employed. The power input of a cell may be reduced by cutting down either the current or the voltage across the cell. The production of aluminum is directly proportional to the current. The voltage drop across the cell is a function of the anode-cathode distance, and at small spacings results in smaller amounts of heat generated due to the resistance of the bath. Lower cell temperatures result, with reduction of the tendency to form metal mist but with increased losses by reoxidation at the anode. With lower cell temperatures, surface oxidation of the carbon anodes by the air is cut down. In general, however, attempts are not made to

secure the greatest electrical or thermal efficiency but to produce aluminum at the lowest cost per pound by striking a balance between current capacity of the cell, voltage drop, anode area, anode current density, anode-cathode spacing, thermal insulation, and purity of anodes when such purity is obtainable without excessive cost. A typical early arrangement of aluminum furnace or "pot" room is shown in Fig. 173; a more modern design is found in Fig. 174. Large-capacity cells are shown in Fig. 171. Operating data are tabulated in Table 69.

TABLE 69. ELECTROLYTIC PRODUCTION OF ALUMINUM

Raw material. . . .	Purified Al_2O_3
Melting point material, °C....	Cryolite 1000
Melting point metal, °C	Al 660 (about)
Bath material....	Cryolite + Na, Al, Ca fluorides
Furnace:	
Shape	Rectangular
Shell.......	Steel
Anode:	
Material.....	Carbon
Arrangement........	Suspended vertically
Cathode material.	Carbon lining
Amperage of cell....	20,000–50,000
Voltage across cell.. 5	5 5–6 5
Operating temperature, °C	900–1000
Concentration of raw material in bath....	2–5 % Al_2O_3
Theoretical decomposition voltage.	2 8
Carbon consumption, lb/lb Al	0.6–0.65
Raw material consumption, lb Al_2O_3 per	
lb Al......................	About 2
Current efficiency, %.......	80–90
Energy efficiency, %......	25–40
Energy consumption, kwhr/lb Al........	8.5–9.5
Sp gr, molten Al......................	2 29 (1000°C)
Sp gr, molten cryolite	2 095 (1000°C)

ALUMINUM REFINING

A practical method for refining impure aluminum in order to produce aluminum of high purity has long been desired. The production of pure aluminum in ordinary aluminum cells necessitates exceedingly close operating control and the use of pure alumina and electrodes, all of which may or may not be obtainable without excessive cost. Ordinary aluminum is 99 per cent
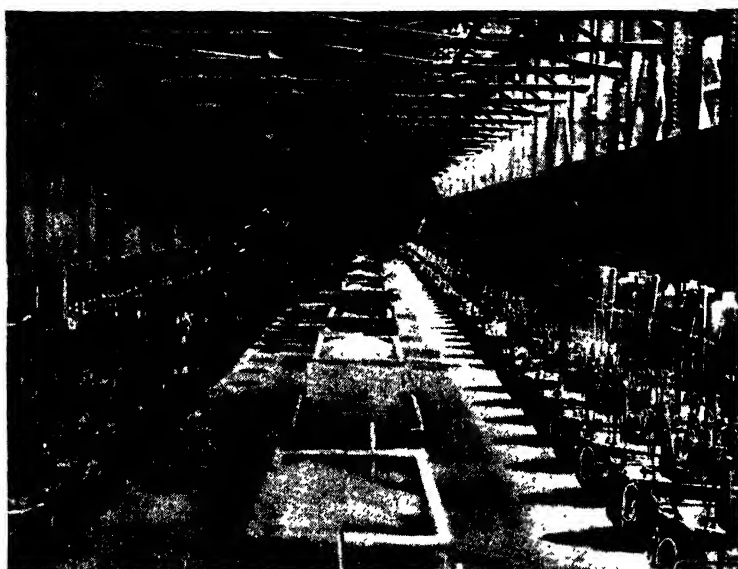
Fig. 173. Early aluminum pot room. (*Aluminum Company of America.*)
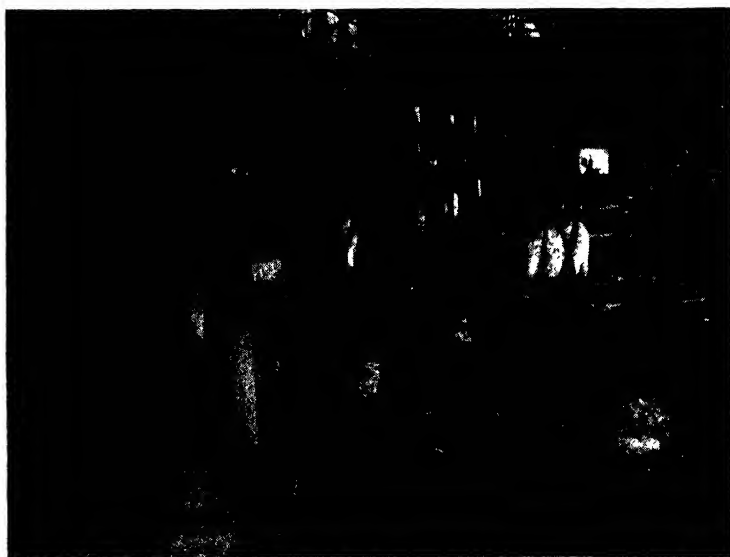
Fig. 174. Aluminum pot room with overhead feed bins. (*Aluminum Company of America.*)

or better Al, and its properties are quite different from electrolytically refined aluminum running 99.8 or better. Metallic aluminum cannot be deposited by electrolysis in aqueous solutions. Organic solvents for the metal have low electrical conductivity and are costly, which factors render their use impractical. The only apparent solution industrially possible lies in the use of a fused salt electrolyte, first proposed in 1900 by William Hoopes.[23]

Cell and Electrolyte. In the refining cell, a molten aluminum cathode floats on an electrolyte heavier than the molten aluminum. The anode alloy, which is heavier than the electrolyte, is at the bottom of the cell, so that the unit becomes an inverted form of the aluminum-producing furnace. The construction is shown in Fig. 175.

The bath is composed of a mixture of cryolite, AlF_3, and BaF_2, nearly saturated with alumina. By virtue of the cooling effect of the side walls of the cell there is built up on these walls by a process of selective crystallization a thick crust rich in alumina. This is very refractory, and not easily dissolved away by the bath if for any reason the temperature of the cell rise above normal. This crust serves to insulate, electrically and thermally, the molten bath from the shell. It also minimizes the leakage of current from anode to cathode through the walls. In starting up such a cell, it is very important that the upper half be maintained in an electrically neutral condition, in order to prevent the formation of a side crust partially contaminated with metal. Such a crust seems to conduct enough current to cause electrolysis to take place in it. Its content of metal gradually increases until its conductivity becomes prohibitively high.

In order to make the electrical connection to the molten cathode, it was found necessary to use graphite electrodes dipping into the floating aluminum layer. These are carried on heavy copper rods, as shown in Fig. 175. It was also found that under proper conditions a crust of frozen bath, rich in alumina, would form over the upper surface of the metal and around the electrodes and act as a protective cover. Care must be taken to maintain an adequate metal thickness in the cathode layer; otherwise the heavy currents and powerful magnetic fields set up a swirling motion so violent that the anode and cathode layers

[23] Hoopes, W., U.S. Patent 673,364 (1901).

can come into contact in spots. This, of course, results in their union and the loss of the refined metal.

Anodes. There seems to be only one practical anode for such a cell. This is a copper-aluminum alloy, low in iron and titanium (which raise its freezing point) and preferably containing enough silicon to lower its freezing point considerably, so that it will remain adequately mobile even when the aluminum content has been largely reduced. The proper working temperature of the
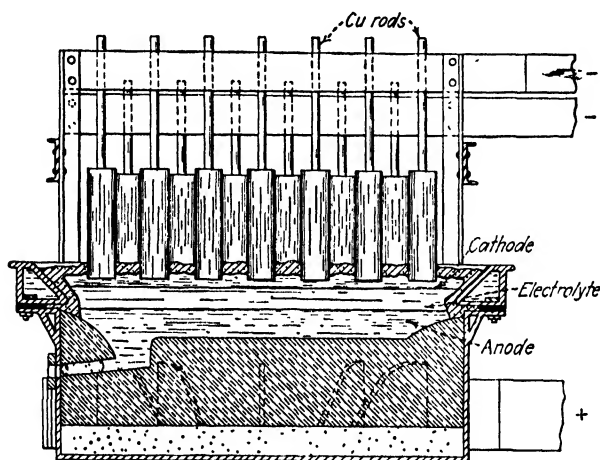
FIG. 175.   Aluminum refining cell.

cell is limited by the properties of the fused electrolyte, and lies between about 900 and 1100°C. In the nature of things, the anode alloy tends to be cooler than the electrolyte. If any appreciable amount of it freeze, copper and other impurities will be dissolved from the frozen portions by the current, and the refined metal will be contaminated.

Cell Operation. The cell is easily started by pouring into it a layer of molten bath several inches thick, lowering the graphite connectors to dip into the bath layer, and turning on full-load current. A layer of molten anode alloy is then slowly poured in, taking care that the joint between the upper and lower halves of the cell is covered only by the bath. A layer of molten aluminum carefully poured on the surface of the bath, followed by a final adjustment of the graphite connectors, completes the operation. If the bath be of proper composition, the alumina-rich

side crust and top crust will soon begin to form. In a few hours the cell is in normal operation.

In order to keep the cell operating, the aluminum produced at the cathode must be tapped off, and a corresponding amount of impure aluminum or aluminum-copper alloy added to the anode. If the cell be employed to refine impure aluminum, this operation may be carried out simply in two steps. The necessary amount of the molten impure aluminum is poured into a suitable crucible which is placed in a hole in the floor in front of the anode alloy tap hole. The current is then cut off, the tap hole opened, and a few hundred pounds of the impoverished anode alloy tapped into the crucible of molten aluminum, so as to produce an alloy heavier than the molten bath. This alloy is then poured back into the cell through a suitable carbon-lined funnel extending into the anode alloy layer. As the level of the molten mass in the cell rises, the tapping trough in the top section is opened, and the pure cathode metal is allowed to flow out into another crucible, the amount obtained being, of course, approximately the same as that of the new aluminum added.

The cells operate with an excellent current efficiency on about 5 to 7 volts and about 20,000 amp. They require little attention except at tapping time. A certain amount of sodium is produced at the cathode and, together with some of the aluminum, is gradually oxidized. This results in a gradual thickening of the side crust. From time to time the excess of alumina is removed by digging out some of this side crust and adding fresh electrolyte. The cells have been operated continuously for months at a time under working conditions. It has been shown to be practical to produce any desired amount of metal with an average purity of over 99.80 per cent. Much of the metal will be 99.90 per cent pure. The grade commercially offered, however, is guaranteed to be 99.80 per cent. The highest purity obtained by electrolytic refining was 99.983 per cent. The principal impurity is usually copper, the iron and silicon being present in very small amounts only.

MAGNESIUM

Metallic magnesium was formerly prepared by two electrolytic methods, one termed the "chloride" and the other the "oxide

process." Both methods will be discussed, although the oxide process is no longer in operation.

Magnesium was first electrochemically prepared by Bunsen in 1852 by the electrolysis of fused anhydrous $MgCl_2$.[24]

Intermittent Chloride Process. Harvey[25] has described the intermittent chloride process. Before the First World War the metal was made in Germany by the electrolysis of fused anhydrous carnallite, $KClMgCl_2 \cdot 6H_2O$, which occurs naturally, has a lower melting point than $MgCl_2$, is less volatile, and can be dehydrated more readily. The fused, anhydrous material was fed into the electrolytic cells[26] and electrolyzed until the magnesium chloride content had been lowered to 10 or 15 per cent. Unfortunately, an electrolytic bath consisting of 85 per cent potassium chloride and 15 per cent magnesium chloride has a specific gravity at 700°C so close to that of magnesium metal floating in it that it is impossible to control the position or level of the metal in the bath. As $MgCl_2 \cdot 6H_2O$, the raw material tends to decompose during dehydration and fusion into MgO or oxychloride. The resulting residue contains MgO. In practice approximately equal parts of NaCl were added to prevent this decomposition. Potassium chloride is more effective, but its greater cost, at least in the United States, precluded its use. Small amounts of NH_4Cl were added to retard the decomposition of $MgCl_2$. The mixed salts were dehydrated, by careful heating in iron pots over a slow fire, until five of the six molecules of water were removed, after which the salts were quickly transferred to a hot quick fire for finishing. The double salts melt to a fairly clear fusion at 620°C and contain about 10 per cent MgO.

In the furnace or cell, as shown in Fig. 176, a cast-steel pot formed the electrolyte chamber and also served as the cathode. A graphite anode was suspended centrally in the fused salt, being provided with means for varying its height so that the bath level which lowered during electrolysis could be followed and a constant voltage on the cell maintained. The furnace cycle was a 24 hr one, at the end of which the residual bath containing about 10 per cent $MgCl_2$ and 90 per cent NaCl was removed and a new molten charge added. Sodium displaces magnesium from its

[24] BUNSEN, R., *Lieb. Ann.*, **82**, 137 (1852).

[25] HARVEY, W. G., *Trans. Am. Electrochem. Soc.*, **47**, 327 (1925).

[26] SHCHERBAKOV, I. G., *et al.*, *Kalit* (*U.S.S.R.*), **5**, 10, 19–28 (1936). .

fused salts, and, within the limits of concentration stated, practically no sodium is electrolyzed. The intermittent nature of the operation and expensive dehydration process are disadvantages of this method of reduction.

The temperature of the electrolyte was maintained, partly by the resistance of the bath to the electric current, and partly by a coal fire maintained under the steel pot.

The reduced magnesium metal was lighter than the electrolyte and rose to the surface, collecting in pools near the edge of the cathode pot. The molten chloride salt formed a protecting film covering the floating metal. At a temperature range between 675 and 725°C, although no separating diaphragm was used in the cell, recombination between magnesium and chlorine was not excessive. In practice it was found best to maintain the supply of external heat as uniformly as possible, and to obtain temperature regulation almost entirely by electric methods.

Magnesium metal was recovered at periodic intervals by opening a door in the front of the furnace hood and ladling out the metal into molds.

FIG. 176. Intermittent chloride process cell.

Special ladles were used with holes in the bottom of such size that the thinner electrolyte drained out. The furnace metal usually carried about 10 per cent of electrolyte which was removed by a further refining or remelting operation carried out in oil-fired steel pots.

Oxide Process. The oxide method, somewhat analogous to alumina reduction, employed an electrolyte of magnesium and barium fluorides in equal parts with sufficient NaF added to make the bath fluid at 950°C. The use of BaF_2 raised the specific gravity of the molten bath to approximately 3.2, which served the double purpose of causing the reduced metal to rise

quickly to the surface and at the same time prevent the MgO, the raw material for electrolysis, from settling too rapidly. Satisfactory operation of the cell could be obtained even with several per cent of impurities such as the oxides of Si, Fe, Ca, and Al. None of the constituents of the bath are hygroscopic. The process is now of only historic interest.

The shell of the furnace (Fig. 177) consisted of a reinforced steel box. Carbon anodes were attached to overhead copper buses. A heavy layer of frozen electrolyte served as a lining as well as a heat and electrical insulator. Cathodes were of cast iron projecting upward through slots in the furnace shell. The bases of the cathode castings were water-cooled in order to ensure complete solidification of the bath at the points where the cathode passed through the shell. The active portion of the cathode was completely submerged, its upper end being about 6 in. below the bath surface. The cell was divided into compartments by two water coils dipping into the bath at the top of the furnace. These divided the furnace lengthwise and formed an anode compartment in the center and two cathode compartments on the sides.

Magnesium oxide was added to the bath around the anodes at frequent intervals. Its solubility in the bath was probably not over 0.1 per cent at 950°C. The electrolyte contained an excess of oxide at all times, held in suspension by the high specific gravity of the bath. There was some constant loss of fluorine in the process, but this loss was not materially greater than that which takes place in aluminum electrolysis. There was a characteristic anode effect evident at times, seemingly the result of an accumulation of fluorine gas on the anode surface.

FIG. 177. Oxide process: double cathode cell. Upper, vertical section; lower, horizontal section.

The metal rose from the cathodes and collected just under the frozen crust of electrolyte at the top of the bath. Here the rising metal could accumulate until such time as it was removed. This

was done by breaking a circular opening in the upper crust and ladling out the molten metal just below. Operating details of the oxide process are given in Table 70. ·

Continuous Chloride Process. The Dow Chemical Company developed a continuous chloride process, described by Gann.[27] Its basic raw material was a salt brine. The process permitted the separation of hundreds of tons per day of a mixture of the chemically allied salts—$MgCl_2$, $CaCl_2$, and NaCl—in addition to the liberation of bromine. These brine constituents, when separated from the $MgCl_2$, became the raw materials for other branches of the local chemical industry. The success of the sea-water process, described later, as well as changes in the utilization of brine, has made the process of only historic interest.

Natural brine pumped from wells 1,200 to 1,400 ft deep contained approximately 14 per cent NaCl, 9 per cent $CaCl_2$, 3 per cent $MgCl_2$, and 0.15 per cent bromine. After the bromine was removed, the brine was treated with a magnesium hydrate slurry to precipitate the iron and other impurities which were separated in continuous thickeners and sedimentation tanks. The decanted liquor was evaporated until the NaCl had crystallized. The salt was removed on rotary filters.

The $MgCl_2$ and $CaCl_2$ in the rotary-filter mother liquor were separated from each other by fractional crystallization. Under controlled composition and temperature conditions, the crystals separating from a complex salt solution may have a different composition from the solids remaining in the mother liquor. This was accomplished by concentrating a solution with a 1:3 weight ratio of $MgCl_2$ to $CaCl_2$, whereupon crystals of the double salt "tachydrite," $2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$, were formed. It has a 2:1 ratio of $MgCl_2$ to $CaCl_2$ but its crystals are in equilibrium with a mother liquor having a $MgCl_2$ to $CaCl_2$ ratio of 1:10. The crystals and liquor were separated in false-bottom tanks. The tachydrite crystals were then dissolved in hot water and the solution transferred to a series of crystallizers where substantially pure $MgCl_2 \cdot 6H_2O$ separated, leaving a mother liquor containing $MgCl_2$ and $CaCl_2$ in a ratio of approximately 1:1. This solution, together with the $MgCl_2 \cdot 6H_2O$ wash water, contained approximately half of the $MgCl_2$ originally present in the brine and was returned to the process for rework-

[27] Gann, John A., *Trans. Am. Inst. Chem. Engrs.*, **24**, 206–230 (1930).

TABLE 70. ELECTROLYTIC PRODUCTION OF MAGNESIUM

	Oxide process		American continuous chloride (Dow Ward cell)		German chloride		
	Electrolyte, %	Feed, %	Electrolyte, %	Feed, %	Electrolyte, %	Feed, %	Sludge, %
Analysis of material:							
$MgCl_2$			25	75	10–25 (av. 15)	86–90	
MgF_2	45						
MgO		99		3		Bal.	30
$NaCl$			60	1	30		
BaF_2	45						
$CaCl_2$			15	0 75	40–50	5–6	
KCl	10				10	Bal.	
NaF							
CaF_2					0 5–1		
H_2O				20			
Metallic Mg			4 5				
Bath dipped per lb Mg							10 (bath 60)
Bath consumption, lb/lb Mg							0.28

	Oxide process	American continuous chloride (Dow Ward cell)	German chloride
Raw material:	MgO	Synthetic $MgCl_2$ · X H_2O	Synthetic $MgCl_2$
Melting point, °C	MgO 2,800	$MgCl_2$ 708	$MgCl_2$ 708
Melting point, metal °C	Mg 651, boiling point 1,120	Mg 651	Mg 651
Cells:			
Material of construction	Steel	Steel	Steel
Shape	Rectangular	Rectangular	Rectangular
Size		11' long, 5' wide, 6' deep	7'4" long, 5' wide, 4' deep

Life, days, refractories		500	Partition 450, lining 1,800
Life, days, steel shell		1,000	2,400
Capacity of electrolyte	950	10 tons	
Temperature of electrolyte, °C		700	
Cell arrangement		108 cells in series	
Current:			
Amperes	9,000–16,000	30,000–70,000	23,000
Voltage per line		600–650	
Voltage per cell	9–16	6 2	7
Current efficiency, %	50–60	75–80	88
Cathodes:			
C.d. amp/sq in		8	4.3
Cathodes	Steel	Steel	Steel
Power:			
D.c. per lb metal, kwhr	14–16		8.0–8.5
A.c. per lb metal, kwhr	20–25		11.2
D.c. power line			Motor-generator sets
Rectifier number and capacity	Motor-generator sets	Rectifiers 6–100,000-amp mercury	
Rating per line per day, lb		100,000	
Rating per pot per day, lb		1,100	
Heating	Internal resistance	External	
Cathode-anode distance, face to face in.			7
Anodes:			
Material	Carbon	Graphite	Graphite
Arrangement	Suspended vertically	Suspended vertically	
Spacing, in.		1½	
Size		8″ diam. × 9′ long	4½″ × 9″ × 55″
Electrode bundle			4½″ × .4″ × 55″
Number per bundle			6
Number per cell		22	18
Life, months			12–16
Consumption, lb/lb metal		0 1	0.025
C.d. amp/sq in.	<40		4 3
Magnesium analysis, %	99+	99 9	99.9
Chlorine concentration from cell			90

ing. The $MgCl_2 \cdot 6H_2O$ crystals were melted in their water of crystallization, and the fused mass was flaked on rotating steel drums.

Feed for the electrolytic cells was prepared by dehydration operations to remove the six molecules of water of crystallization. Air drying is practical to a composition corresponding approximately to $MgCl_2 \cdot 2H_2O$ provided the temperature is controlled to prevent incipient fusion. In earlier practice the last two molecules of water were removed by heating to still higher temperature in an HCl atmosphere which is necessary to prevent hydrolysis and the formation of MgO.

The magnesium metal formed is lighter than the cell bath and therefore rises and floats on the surface of the same. It does not burn because of the protecting action of a thin film of the molten salt bath. On the other hand, the sludge which forms during the normal operation of the cell is heavy and immediately sinks. This sludge is due largely to the small percentage of MgO present in the cell feed. This automatic separation of metal and sludge, the high purity of the cell feed (less than 0.01 per cent heavy metal impurities capable of affecting the quality of the metal), the freedom from contamination due to chemical attack of the magnesium on the cell parts, and finally, the washing and purifying action of the cell bath itself, all combine to yield a metal of such purity that subsequent refining is unnecessary. The average analysis of this magnesium direct from the cells reveals a purity of 99.9 per cent, a figure that at times rises to 99.95 per cent. The minute traces present consist of silicon, iron, aluminum, and manganese.

Ward, Hunter, and others[28] have patented cells for magnesium chloride electrolysis with collecting chambers as well as with a "louver type cathode with inclined surfaces sloping upwardly away from the anode," or with troughs ranged one above the other to entrap molten metal rising from a cathode surface and keep it away from anodic chlorine.

Figure 178 shows a general view of a bank of cells in a modern plant.

The cell feed, as described by Hunter,[29] is $MgCl_2 \cdot 1.25 \ H_2O$

    [28] Ward, L. E., and Hunter, R. M., U.S. Patents 1,828,004; 1,828,006; 1,828,022; 1,851,789; 1,863,385; 1,921,376–7.
    [29] Hunter, Ralph M., *Trans. Electrochem. Soc.*, **86**, 21–32 (1944).

(75 per cent $MgCl_2$) in granular form. The commercial electrolysis of pure, or even approximately 100 per cent, $MgCl_2$ baths has probably never been tried. ·Its melting point is high (712°C). The electric conductivity is low, and the fact that additions of other chlorides—notably of the alkali and alkaline earth groups, all of which have higher decomposition potentials than magnesium chloride—lower the melting point of the mixture and improve the conductivity suggests the use of mixtures

FIG. 178.   Bank of magnesium cells.   (*The Dow Chemical Company.*)

for electrolysis.   As a result, most fused baths contain a minor quantity of magnesium chloride and consist in the main of sodium or potassium chlorides.   It must be borne in mind that the composition of the molten electrolyte is dictated by the impurities. The exact composition of the fused bath used in an electrolytic magnesium process is dependent on the raw materials available in the locality.

Michigan brines used for the production of magnesium contain magnesium chloride, sodium chloride, calcium chloride and, present in very small amounts, strontium chloride.   These Michigan brines contain little potassium chloride and practically no sulfates.   In the electrolysis of magnesium chloride, sodium chloride is preferred to potassium chloride.   Its conductivity is greater, and it has the advantage of yielding a bath with

higher specific gravity, thereby facilitating satisfactory separation of the magnesium metal. Since the Midland raw material contained calcium chloride, it was practically impossible to operate a process without the effects of calcium. All impurities added to the cell leave in one of the following ways: by removal in the magnesium metal produced; by removal in the chlorine-rich anode gases; by removal in the cell sludge; or by the intentional "dipping" of the bath for the control of composition.

Magnesium produced in the cell will remove those impurities which alloy with it. These include aluminum, copper, nickel, zinc, silicon, and to a small degree manganese, all of which deposit and alloy with the magnesium produced at the cathode or are reduced by chemical reactions in the bath adjacent to the cathode. As these metals are undesirable in the virgin magnesium metal, however, care must be taken to prevent their being included in the cell feed. Fortunately, most of the metals are not present in the raw materials and may be kept out of the cell feed by judicious elimination of them in the chemical processing preceding electrolysis.

Other metals such as iron, boron, and to a lesser extent manganese, are either liberated on the cathode or their compounds are reduced by the magnesium floating in the cell bath. Since these metals do not appreciably alloy with the magnesium, they fall to the bottom of the cell. If cell operating conditions are not correct, these metal impurities may form shells around small particles of magnesium, resulting in globules whose net specific gravity is greater than that of the bath, and which will therefore fall to the bottom of the cell, and the magnesium in these globules will be lost. Proper operation should permit the formation of larger globules which tend to rise to the top[30] where shells of heavy metal are sloughed off and fall to the bottom.

The magnesium oxide (from hydrolysis of $MgCl_2$ in the feed) introduced into the cell follows several courses. A limited amount dissolves in the bath and may be electrolyzed; a considerable portion is rechlorinated to magnesium chloride, probably due to the presence of chlorine, carbon, and carbon monoxide; and the remainder, amounting to less than half of that added, falls to the bottom of the cell. With the heavy metals and shell-encased magnesium, MgO forms a spongy layer disposed

[30] OETTEL, F., *Chem. Z.*, **61**, 156 (1937).

throughout the bottom of the cell. This "sludge" is dipped out periodically. A typical sludge analyzes 18 per cent MgO, several per cent Mg, less than 1 per cent heavy metals, and the balance consisting of bath which is interspersed through the sponge. The bath thus enclosed in the sponge is the principal means of escape for the soluble impurities of alkali and alkaline earth groups which are not affected by the electrolysis and which would otherwise accumulate in the bath. Any other adjustment of materials in or out must be accomplished by the addition of the desired salt and ladling of the bath.

Sulfates combined with the alkali or alkaline earth metals are detrimental. The possible reactions which may be written for the behavior of sulfates in the magnesium cell range from the reduction[31] of the SO_4 radical in the neighborhood of the cathode by magnesium to elementary sulfur or SO_2; the appearance in the sludge of iron sulfides: or the liberation of SO_2 and oxygen on the anode.

The unusual difficulties encountered in attempts to separate calcium completely from magnesium, as either oxides, carbonates, or chlorides, mean that when dolomites are used as a raw material, some calcium chloride will be present in the feed delivered to the cells. This makes it necessary to adopt a bath composition in which calcium chloride is a major component. The electrochemistry of magnesium permits operation in most of the systems involving calcium, sodium, potassium, and magnesium.

The flow sheet for the production of magnesium from sea water is shown in Fig. 179.[32] The process consists of the following steps: (1) Precipitation of magnesium hydrate from sea water using milk of lime made from oyster shells. (2) After filtration, the hydrate is converted into magnesium chloride using 10 per cent solution of hydrochloric acid. (3) The magnesium chloride solution is concentrated, first in direct-fired evaporators, then on shelf driers, and finally in a rotary drier. (4) Flaked magnesium chloride, in practically anhydrous condition, is fed into the cells where it is electrolyzed to produce metallic magnesium of average purity between 99.9 and 99.95 per cent, along with by-product chlorine which is used to make HCl.

The chief impurities to be found in the cell feed made from sea

---

[31] OETTEL, F., *Z. Elektrochem.*, **2**, 394 (1895).

[32] KIRKPATRICK, S. D., *Chem. & Met. Eng.*, **48** (No. 11), 76, 130 (1944).

water are sodium chloride, calcium chloride, and small amounts
of potassium chloride. Sulfate is present, but it may be kept
low. Other impurities are present in very small quantities.

An element which caused considerable trouble in cell feed made
from ocean water is boron. The vapor pressure of halides of
boron, particularly the chloride, is high, so that more than 70
per cent of the boron is vaporized as boron chloride in the anode
gases and later condensed in the hydrochloric acid solution which
is formed. Boron may accumulate in the cell feed produced from
precipitated ocean-water magnesium hydrate reacted with the
recycling hydrochloric acid.

In a pure salt bath operating on boron-free feed, the deposited
magnesium leaves the cathode in small spheres which do not
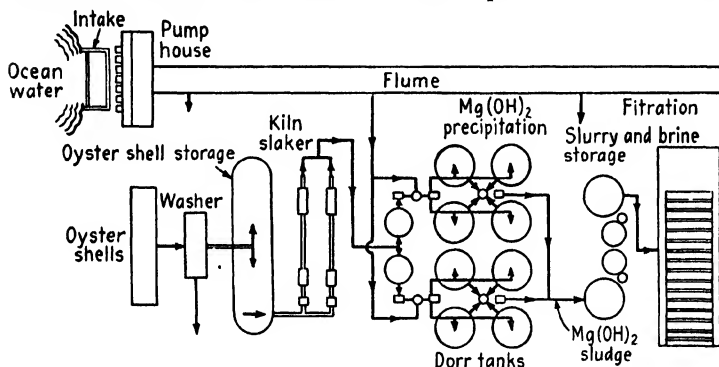
FIG. 179. Flow sheet of magnesium production

coalesce even when strenuously agitated or puddled. Oettel[33]
reported this phenomenon as early as 1895 and suggested its
remedy by the addition and maintenance of small quantities of
calcium fluoride, which is soluble in the bath and probably dis-
solves films which may form on the surface of the magnesium
spheres.

The presence of boron in cell feed results in liberation of boron
at the cathode, where it is believed to react with the magnesium
to form metallic borides. This metallike deposit collects between
crystals and exerts a dispersing action on the metal which is
impossible to control with calcium fluoride. Less than 10 ppm
of boron in cell feed is not particularly troublesome, but if

[33] OETTEL, *loc. cit.*

100 ppm are present things begin to happen. The result is a mass of uncollectible metal, some of which is sufficiently weighted down by the presence of boride to sink and accumulate in the sludge at the bottom of the cell. Sludge formations many times normal result, cell operation deteriorates, the magnesium metal will not coalesce, and production efficiency falls. Boron is best
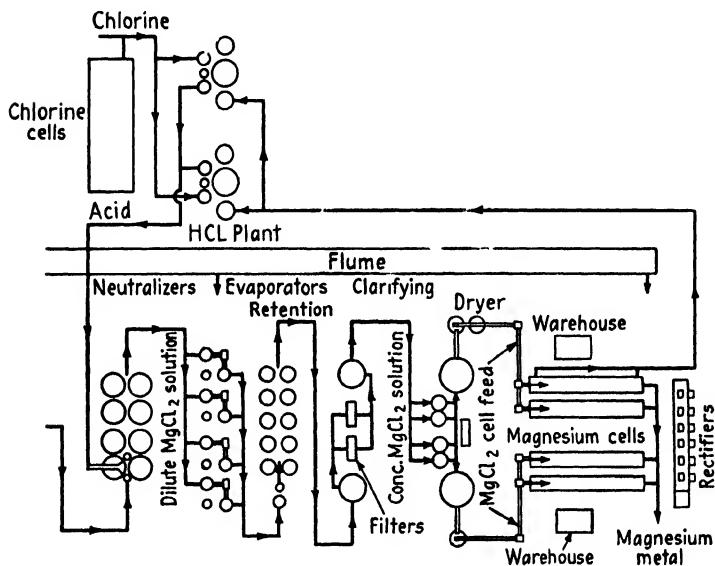
from sea water.   (*Chemical Engineering.*)

controlled by keeping it out of the cell feed, which is accomplished by chemical treatment of the weak magnesium chloride liquors.

The operating data of the Dow Ward cell[34] are given in Table 70. Figure 180 shows a front view of the top of a cell, Fig. 181 a side view, and Fig. 182 an end view.

The cells are externally heated to maintain the bath temperature of 700°C. External heating provides a flexibility so that load reductions and shutdowns may be taken care of without "freezing" of the electrolyte.

With slow and uniform addition, cell feed containing 10 to 20 per cent water may be introduced as most of the water flashes off immediately.

[34] U.S. Patent 1,921,377.

The feeding of the cell is almost continuous except for metal dipping, which is best accomplished on a nonfeeding cell and is usually performed two or three times a day. Sludging is performed once a day. Twenty-two graphite anodes, 8 in. (203 mm) in diameter and about 9 ft (2.7 m) long, are suspended into the cell from above the refractory cover. The presence of water in the feed means the presence and electrolysis of some water in the
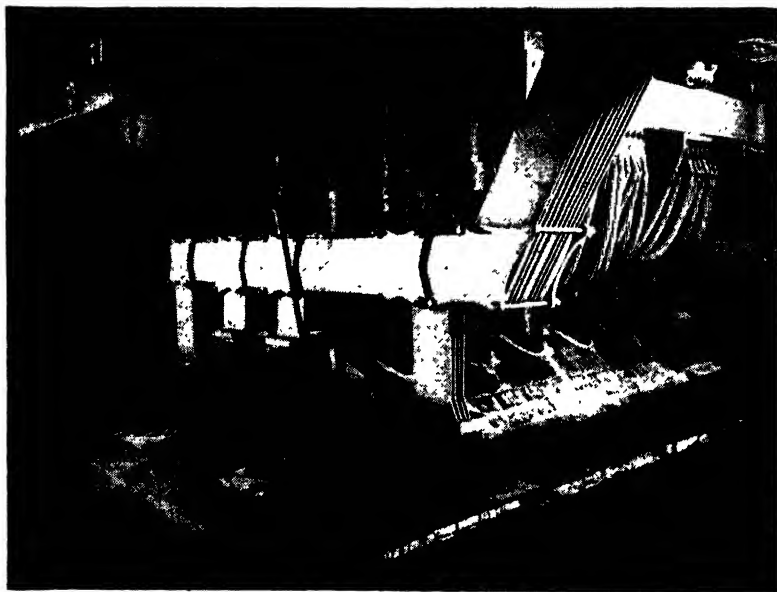
FIG. 180. Close-up of magnesium cell, front view. (*The Dow Chemical Company.*)

bath. This is evidenced by the liberation of hydrogen at the cathode and the consumption of the anodes by oxygen, which, together with the anode scrap, amounts to 0.1 lb graphite per pound of magnesium metal. The anodes must be adjusted daily.

The buildings housing the cells are built practically around the cell for the purpose of providing adequate ventilation and at the same time protection from the weather. The air used for the ventilation of the cells may be as high as 60,000 cu ft per min per cell.

The collection of the metal is accomplished by inverted troughs placed under the bath level, which catch the metal as it rises from the cathodes. These troughs direct it to metal wells situated in

the front of the cells, from which it is dipped two or three times daily.

Direct current for the cell pot lines is furnished by six 10,000-amp, single-anode tank, ignitron-type rectifier assemblies operating in parallel to give 60,000 amp on the bus.   The operating

Fig. 181.ᐧ Close-up of magnesium cell, side view.   (*The Dow Chemical Company.*)

voltage range of the rectifier may start as low as 65 volts without phase angle control and has a maximum of 650 volts.   For short starting periods, voltages lower than 65 volts may be desired and are obtained.   The decomposition potential of magnesium chloride is 2.6 volts, meaning that with 100 cells in series 260 volts corresponds to zero current.   This makes it unnecessary to go below 260 volts for usual operations.   Cells once placed on the line operate over 500 days, though the pots usually

give two such periods. When interruptions for putting cells on or off are required, the current is dropped a few thousand amperes, while the cell is being "jumpered" out. A pot line or series requires about 475 tons of 0.5 by 9 in. (13 by 229 mm) copper busbar, which is used in cross sections of 81 sq in. for the carrying of 60,000-amp load.
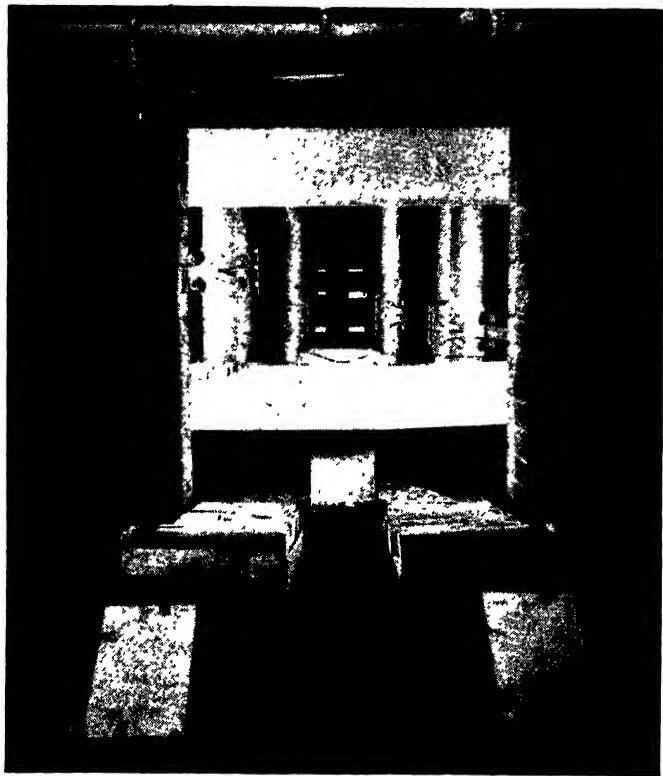
Fig. 182. Close-up of magnesium cell, end view. (*The Dow Chemical Company.*)

The anode products of the cell are chlorine, hydrogen chloride, and carbon dioxide, totaling 7 to 10 per cent by volume and decreasing in the order named. They are removed from the cell with a large amount of inleaking air. A suction of 0.25 in. (6.4 mm) water pressure is maintained at the cells. The high temperature of these gases makes it necessary to conduct them a short distance in brick, and then quench with water in a short section of graphite pipe to a temperature sufficiently low to be

handled in Haveg[35] acid-resistant pipe. The Haveg lines run the length of the buildings and deliver to the furnaces operating for the use or disposal of gases in most plants.

Anode gases are converted to hydrochloric acid which is used as such, or employed to neutralize magnesium hydrate, prepared from sea water, or dolomite for the production of cell feed. The production of hydrochloric acid from these dilute gases is accom-
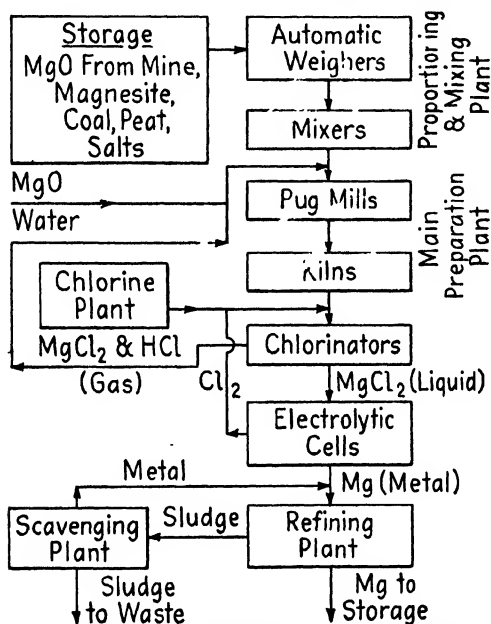
FIG. 183. Flow sheet of Basic Magnesium, Inc., main reduction works.

plished by first removing the hydrogen chloride from the gas with water scrubbing. The remaining chlorine, together with several times its volume of water vapor, is heated to at least 1,000°C in a gas- or oil-fired regenerative furnace. The conversion is about 95 per cent, and the hydrogen chloride is absorbed to form 20 per cent hydrochloric acid, which is used for the neutralization. Towers, fans, and ducts are usually made of rubber-lined steel, and precautions are taken to keep temperatures within the safe range for rubber.

Cell metal is usually weighed and inspected in the cell build-

[35] Composed of asbestos fiber and a phenol-formaldehyde resin; sp gr, 1.6.

ings and transferred to warehouses or to the alloy department. The standard shapes are 16-lb (7.2-kg) notch bar ingot, and a 4 by 16 in. round ingot weighing 12 lb (5.4 kg).

During the Second World War, a large magnesium plant was built by Basic Magnesium, Inc., at Las Vegas, Nev.,[36] starting with dolomite containing 40 per cent or more MgO, according to the flow sheet in Fig. 183.

The chlorinators consisted of refractory-lined steel shells electrically heated by inserted carbon electrodes to 850°C. The
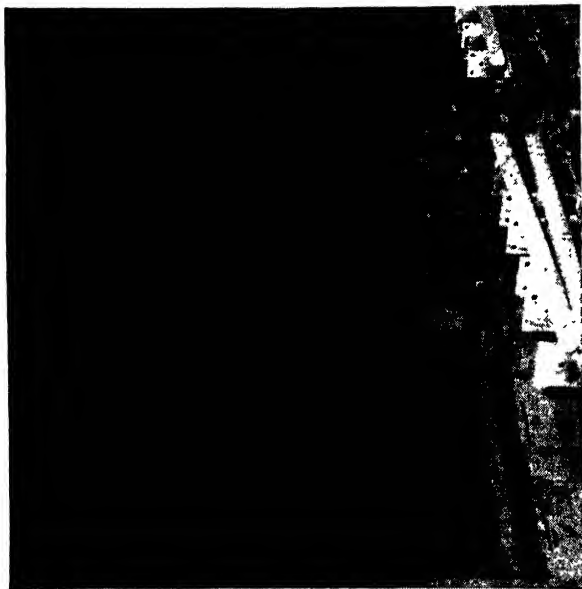
Fig. 184.   Cell construction.   (*Chemical Engineering.*)

MgO was reduced by the coal of the charge to metal, which in turn reacted with chlorine from electrolytic cells to form $MgCl_2$. This collected at the bottom of the furnace and was tapped off for cell feed.

The cells were arranged in 8 rows of 11 each and were of 20,000-amp capacity. Cell construction is shown in Fig. 184, and the operating unit in Fig. 185. Tanks were of steel, but the entire lining was of a refractory material. Through the

[36] RAMSEY, ROBERT H., *Chem. & Met. Eng.*, **50**, 98–101, 115 (October, 1943).

covers of the cells projected six steel cathodes, three graphite anodes, and an exhaust pipe through which chlorine left the cell. The gas escaped at the anodes and was caught by shields which enclosed the anodes to a depth well below the electrolyte surface. Magnesium metal formed at the unshielded cathodes and gradually collected in a pool on the surface of the chloride.   When this condition was reached, the molten metal was manually
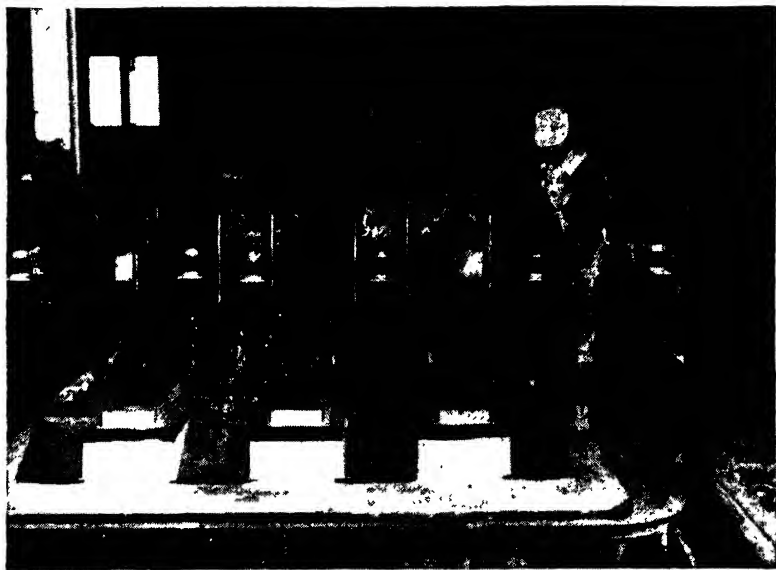
FIG. 185.   Cell for production of magnesium.   (*Chemical Engineering.*)

dipped out into a gas-heated ladle for transfer to the casting operation.   Thereupon more chloride was poured into the cell and the cycle was repeated.   Magnesium was removed from each cell about once a day.

At Basic Magnesium, Inc., the electrolytic procedure was simplified to the extent that the chlorinators produced anhydrous $MgCl_2$.   Current efficiency of the electrolysis was stated to be over 85 per cent.

German Practice.   Procedures at the Bitterfeld and Stassfurt works are typical.   The raw materials for the operation were carnallite from Stassfurt, and high magnesium content dolomite (stated to be 40 per cent MgO).   The dolomite was calcined and slaked in 26 per cent $MgCl_2$ brine, an end product of the

potassium chloride operations from carnallite. The precipitated $Mg(OH)_2$ was filtered on an Oliver filter, washed with water, and cake dropped with 50 to 60 per cent H_2O. This cake was dried at 500°C in a shelf drier with rabble arms on a vertical shaft to move the material across the shelves. It was then calcined at 900°C with "braunkohle" producer gas. The dried MgO was mixed thoroughly with crystal $MgCl_2 \cdot 6H_2O$ obtained by evaporation of the $MgCl_2$ liquors from carnallite. The product, a mixture with analysis $MgO \cdot MgCl_2$ plus 30 per cent H_2O of crystallization, was called "oxychloride" and does not absorb much water. At the magnesium plants it was mixed with braunkohle, which was ground to 25 per cent through 250 mesh. At Bitterfeld the mix was oxychloride 88 per cent, plus coal to give 6 per cent carbon, and peat to yield 6 per cent carbon.

At Stassfurt 12 per cent carbon was obtained from braunkohle; no peat was added. The oxychloride, coal, and peat were mixed in dry mixers, a little $MgCl_2$ liquor added to aid in briquetting, and the moist mixture extruded through a screw briquettor to a $1\frac{1}{2}$-in. cylinder of low strength which broke into 2- to 4-in. lengths as it was extruded. These were dried at 400°C to harden, and then calcined to coke the coal and peat. The product contained about 10 per cent H_2O. The chlorinators at Bitterfeld are each rated at 10 tons of anhydrous $MgCl_2$ per day. They are vertical steel cylinders, acid brick lined, and are 20 ft high, about 9 ft inside diameter, and 13 ft outside diameter. The briquettes were fed in at the top. Chlorine from the cells (90 per cent concentration), to which was added make-up chlorine from liquid, was introduced just above the bottom. The temperature was maintained by carbon resistors operating three phase at 2,500 amp and 22 volts (about 0.6 kva per lb of magnesium). Each chlorinator served about 12 cells. Molten magnesium chloride flowed out of the chlorinators and was transferred into crucibles with tilting mechanism and fed to the cells once per 8-hr shift.

The chlorine losses in this operation result from stack loss of the gas not absorbed in the briquettes, the conversion of CaO impurities to $CaCl_2$ (present in the feed up to 6 per cent), and the conversion of a large portion of the 10 per cent of H_2O to HCl due to the water-chlorine reaction at the elevated temperature. The $CaCl_2$ and the HCl loss are estimated at 0.2 lb of

chlorine per pound of metal for the $CaCl_2$, and 1.5 lb of chlorine per pound of metal for the HCl.

Liquid chlorine was supplied to the process at the rate of 0.5 to 1.0 lb of chlorine per pound of metal. The chlorine balance, therefore, would appear to be 1.48 lb of chlorine per pound of metal in the $MgCl_2 \cdot 6H_2O$ added and 0.5 to 1.0 new chlorine, making a total addition of 1.98 to 2.48 and a known loss from HCl and $CaCl_2$ of 1.7.

The cells are composed of high-silica, acidproof brick built into walls about 18 in. thick and encased in steel shells with solid bottoms. The diaphragm brick is the same composition as the lining (about 70 per cent SiO_2, 30 per cent Al_2O_3). It has a life of about 16 months maximum. The cell pot lining lasts about 5 years. A diaphragm repair requires that the cell be shut down, which includes dipping out the bath. Cells are spaced with about 3 ft between cells in rows about 12 ft apart.

The anodes are graphite pieces about $4\frac{1}{2}$ by 9 by 55 in. and are assembled close together at the top on busbars to make an electrode $4\frac{1}{2}$ by 54 by 55 in. The anodes are sealed into the dome with asbestos and cement, and it is not necessary to renew the seal. The electrodes are never moved during operation except for breakage.

The cathodes are steel castings of eccentric shape designed to present a face about 18 by 50 in. to the anode and tapered up to maintain constant current density through the steel. The bars coming through the top are 3 to 4 in. thick. The spacing is about 7 in. anode to cathode face.

Operating data are given in Table 70 under German practice.

Cells were started by pouring in a few hundred pounds of molten carnallite. The graphite electrodes were temporarily connected to a special transformer for a.c. heating which was used until the cell was full of normal bath, added slowly. There was no indication of iron pickup during the start.

The chlorine gas outlets are one per dome, three per cell. They are about 2 in. inside diameter and are composed of a section of ceramic pipe delivering into a cast-iron line. The line suction was 1 in. of water, and the cell suction about 0.1 in. Before compression, the chlorine was dry-filtered through thimbles (baghouse) of asbestos cloth for removal of the dust and was then compressed to about 20 in. of water pressure with a

blower and returned to the chlorinators. The four cathode chambers are ceramic-covered, with lids provided in the front for metal and sludge removal, and are vented at the back through lines similar to those for chlorine, to remove HCl. These gases were scrubbed and thrown away.

Labor figures were given for operation (cells only) as 20.5 man-hours per ton of magnesium; for maintenance of cells, 16.8 man-hours per ton of magnesium; making a total in the cell room of 37.3 man-hours per ton of metal.

Metal dipping from cells was done once a day and could be done on a 2-day schedule. The metal collected in the four cathode compartments (two double and two single) and was collected by automatic skimming.

The Stassfurt cells are the same as at Bitterfeld with the following exceptions. One line of cells operated at 32,000 amp and 6.8 to 7 volts per cell. These cells contain four anode assemblies and five cathodes (two single and three double). The units are the same, but the cathode-to-anode spacing was given at 4 in. compared to the smaller cells at 7 in. This cell was developed in 1938. Its power requirement is slightly better, being 7.8 d.c. kwhr per lb of metal.

At Stassfurt, d.c. power was supplied by rectifiers of multi-anode type, rated at 6,000 amp, each containing 18 anodes The efficiency was 94 per cent.

A sludge treatment was used to recover the 10 per cent metal in sludge. A pot setting was used with alternating current used on several electrodes. Sludge was agitated in the cell bath. It was claimed that 8 to 10 metric tons of metal were recovered per month.

Composition of the cell bath at Stassfurt was given as 30 to 40 per cent $CaCl_2$, 20 to 25 per cent KCl, 20 per cent NaCl, 15 per cent $MgCl_2$, with about 100 lb of NaF added per cell per month.

SODIUM

In its early history sodium was important only as a reducing agent in the preparation of other light metals, as aluminum. Since that time, however, it has come into its own in other applications and uses: as an alloying material, a deoxidizing agent in light alloys, a "modifying" agent particularly in alumi-

num and magnesium alloys; as a raw material for the manufacture of sodium cyanide, sodium oxide, sodium peroxide, which in turn may be used in connection with the manufacture of oxidizing agents such as the perborates; as well as uses of sodium metal in miscellaneous applications in the synthesis of organic compounds.

Metallic sodium is made in large quantities by the electrolysis of NaOH or NaCl. For many years only the former was used as a raw material. Satisfactory cells have been developed so
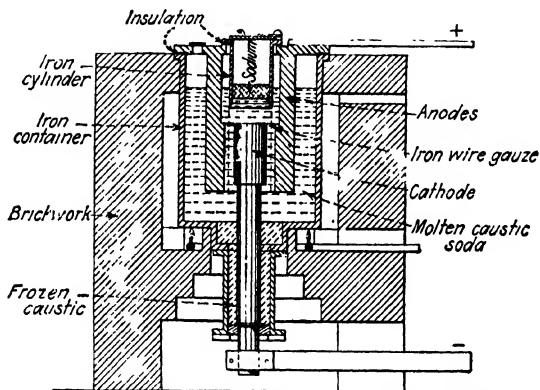
Fig. 186. Castner cell for the production of sodium.

that NaCl has largely replaced NaOH as a starting substance for metallic sodium.

Castner Process. Formerly the most important cell for the production of sodium from NaOH was that of Castner, shown in Fig. 186. The cell consists of an iron vessel mounted in a brickwork furnace so that it might be heated externally. At the bottom the vessel is provided with one or more base pipes or extensions in which the cathode is located vertically, being held in place by solidified caustic around it. Suspended directly above the cathode is an iron cylinder with a cover from which depends an iron-wire gauze diaphragm, completely surrounding the cathode and being located about midway between the cathode and anode. The anodes are in the form of bars dependent from the cover, or the anodes and the cover may be cast in one piece. The small cylinder directly above the cathode serves as a sodium-collecting chamber from which the liquid sodium metal is ladled

out. Caustic is fed into the anode compartment of the cell through an opening in the cover. The gauze diaphragm prevents sodium metal particles from passing to the anode.

The electrolysis of NaOH takes place at a constant temperature not exceeding 20° and preferably at 10° above the melting point of the material. This low value is necessary since sodium metal will redissolve and combine readily at higher temperatures. The melting point of pure NaOH is 318°C, which impurities can bring down to 300°, so that electrolysis is most conveniently carried out at 310 to 320°C. Sodium yields equal to the theoretical are obtained when the temperature of the NaOH is held within 5° of its melting point, while 90 per cent or the greatest commercial yield is obtained at 10° above the melting point of NaOH. With increase in temperature the yield decreases, and at about 20 to 25° above the melting point the rate of recombination of the sodium is about equal to that of the decomposition of hydroxide; no metal is produced.

At the beginning of electrolysis, until all the water of the caustic has been decomposed, hydrogen and oxygen alone are given off. Sodium and hydrogen are then deposited at the cathode, oxygen at the anode. Great care is required to prevent recombination of these elements because of the resulting explosion. It is important that the caustic alkali used be as free as possible from salt. When large amounts of NaCl are present, the bath fouls rapidly because of the attack on the iron parts of the cell. Under any conditions the impurities build up in the cell so that the electrolyte must be changed periodically. Impure electrolytes become viscous and conduct badly. Increase in the necessary voltage and temperature, and decrease of yield, result.

Commercial cells are small, a size formerly commonly employed containing 250 lb of molten NaOH, operating at 1,200 amp at 5 volts, at about 45 per cent current efficiency. The cell proper was about 18 in. in diameter and 2 ft deep. The cathodic current density was 2,300 amp per sq ft (250 amp per dm²).

The reactions of the cell are given as

$$2NaOH \rightarrow 2Na^+ + 2OH^-$$
$$4OH \rightarrow 2H_2O + O_2$$
$$2Na + 2H_2O \rightarrow 2NaOH + H_2$$
$$H_2O \rightarrow H^+ + OH^-$$
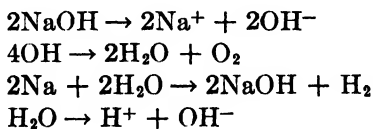
The last equation is the most important source of loss, but if as the result of high temperatures sodium migrate to the anode, it may unite there with the oxygen to form Na_2O_2, which in turn might react with more sodium to form Na_2O, which reacts with water to form hydroxide. In addition, sodium may dissolve in the melt and cause loss.

In a process such as the Castner, the maximum current yield will not exceed 50 per cent, inasmuch as there is one equivalent

FIG. 187. A commercial sodium-producing plant employing modified Castner cells. (*Krebs & Co., Berlin.*)

of water for two of sodium. In practice a 40 per cent yield is more often the case.

A commercial sodium-producing plant employing modified Castner cells is shown in Fig. 187.

The sodium which dissolves in the melt at high temperatures evidently exerts a depolarizing effect at the anode. This was found by Le Blanc and Brode[37] to be so great that oxygen evolution occurred only at high current density. The gas formed at the anode was a mixture of equal parts of hydrogen and oxygen. When a cell produces little sodium and has frequent explosions, the melt is dissolving too much sodium as a result of excessive temperature. The anode is partly depolarized in consequence,

[37] LE BLANC, M., and BRODE, J., *Z. Elektrochem.*, **8** (1902).

and the reaction between the sodium and the moisture present forms mixtures of explosive gas. At low temperatures hydrogen is evolved at the cathode, whereas at high temperatures it appears at the anode. Its visibility at high temperatures is controlled by the current density.

Sodium peroxide dissolved in the caustic produces a depolarizing effect at the cathode which is similar to that of sodium at the anode. The absence of any such depolarizing agents in a pure caustic soda melt causes the passage of only small currents through the electrolyte at low voltages. The peroxide present at the anode and the dissolved metallic sodium at the cathode exert a depolarizing action for the other electrode. As electrolysis continues, the reaction

$$Na_2O_2 + 2Na = 2Na_2O$$

occurs. If water be present at the anode, the following will occur:

$$Na_2O + H_2O = 2NaOH$$
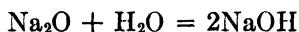
in addition to a direct action of a part of the sodium on the water. The melt will thus be saturated with either sodium or Na_2O_2, depending upon the relative activities of the reactions. However, by permitting fresh electrolyte to flow from anode to cathode or the reverse, anodic or cathodic polarization is effected as desired.

On an assumed decomposition voltage of 2.25 and a current efficiency of 40 per cent, the efficiency of the Castner process is about 18 per cent and the energy consumption 14,600 kwhr per ton of sodium.

Sodium from Sodium Chloride. A large number of cells have been proposed to produce sodium metal by the electrolysis of fused salt, some of which were so complicated that they could not be worked under the temperatures and conditions necessary for operation. Pure NaCl melts at 805°C, impure material as low as 775°. Sodium metal boils at 877°C, and at 800° it has a very high vapor pressure. Even at 600° its vapor pressure is so high that it burns briskly and must be protected from oxidation. This complicates the apparatus considerably. Materials of construction of the cell, particularly of a nonmetallic nature, which will resist the reducing action of sodium metal at 600°, are limited in number. The metal is very fluid and finds its way

into the smallest cracks. The solubility of sodium metal in fused salt electrolytes at 500 to 600°C is small. Above this temperature it increases markedly, and at 700° and above the formation of sodium metal fog in the electrolyte is so great that it is not possible to deposit metallic sodium. The electrolytes employed are those to which additions have been made to bring the melting point 200 to 300° below the melting point of salt.

Smith and Veazey[38] proposed an electrolyte of 35.6 parts NaCl, 64.4 parts Na_2CO_3 by weight, which has a melting point
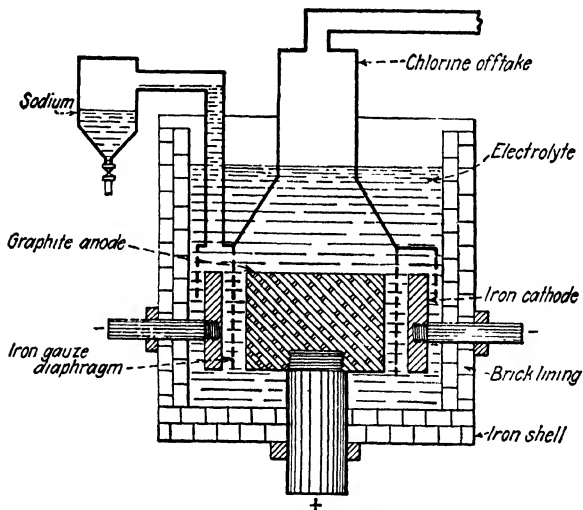
FIG. 188. Downs cell (NaCl).

of 600° and which upon electrolysis in a Castner cell produced metallic sodium. Pfleger and Ott[39] patented modifications of the Castner cell to adapt it to the electrolysis of NaCl. Diaphragms of the wire-net type were used between the anode and cathode, and domes or collecting chambers as in the Castner cell were employed for the sodium. The space between the outer wall of the sodium-collecting chamber and the inner wall of the anode was lined with a material to resist the action of chlorine, the space being employed as a chlorine dome. In the McNitt cell[40] the collecting chamber of the Castner cell is elon-

[38] SMITH, A. W., and VEAZEY, W. R., U.S. Patent 1,334,179 (1920)

[39] PFLEGER, J., and OTT, F., U.S. Patents 1,186,936-7 (1916).

[40] McNITT, R. J., U.S. Patent 1,214,808 (1917).

gated so that a hydrostatic head may be maintained on the liberated sodium metal, the entire cell being closed and used for the electrolysis of NaCl.

The Downs cell,[41] shown in Fig. 188, employs the electrode rising through the bottom of the cell at the center as the anode and superimposes a chlorine-collecting dome. The cathodes are at the side of the cell. Diaphragms are used as in the Castner cell and the sodium collected in hoods in which a hydrostatic head is maintained as in the McNitt cell. Sealing the electrodes where they enter the cell is accomplished by the use of solidified electrolyte. Anode current densities are lower than those at the cathode; otherwise anode effects will be introduced. Faces of the electrodes are parallel. The cell body is iron, lined with a refractory brick. The cathodes entering through the sides are of iron, the anode of graphite. The chlorine-collecting dome is either of iron or iron coated with a ceramic material, or of clayware. The Downs cell is open at the top at which point new electrolyte or electrolyte constituents can be fed in. Operating temperatures are of the order of 600°C. The current furnishes the thermal energy for the cell to keep the electrolyte molten. Current efficiencies are of the order of 75 to 80 per cent. The voltages necessary are higher than those in the Castner cell, and the energy consumption is smaller. Operating data on 24,000- and 32,000-amp German cells are given in Table 71. American cells are larger and operate at higher currents up to 50,000 amp. The furnace is shown diagrammatically in Fig. 189.

The advantages of NaCl electrolytes over NaOH lie in the facts that cheaper raw materials are employed and a by-product chlorine gas is obtained.

The German cells are vertical, cylindrical, steel shells with acidproof brick and covered with removable insulation. The steel shells are 1,632 mm (63.6 in.) outside diameter, 2,016 mm (78.6 in.) high, and are set in holes in the operating floor, so that the upper rim is 924 mm (36 in.) above the floor. A graphite anode enters through the bottom and is surrounded by a concentric cast-steel cathode. Between the anode and cathode there is a diaphragm of iron and steel hanging from an inverted trough which collects the liberated sodium. Chlorine rising from the anode is. collected in a brick-lined nickel dome in the center

[41] Downs, J. C., British Patent 238,956 (1924).
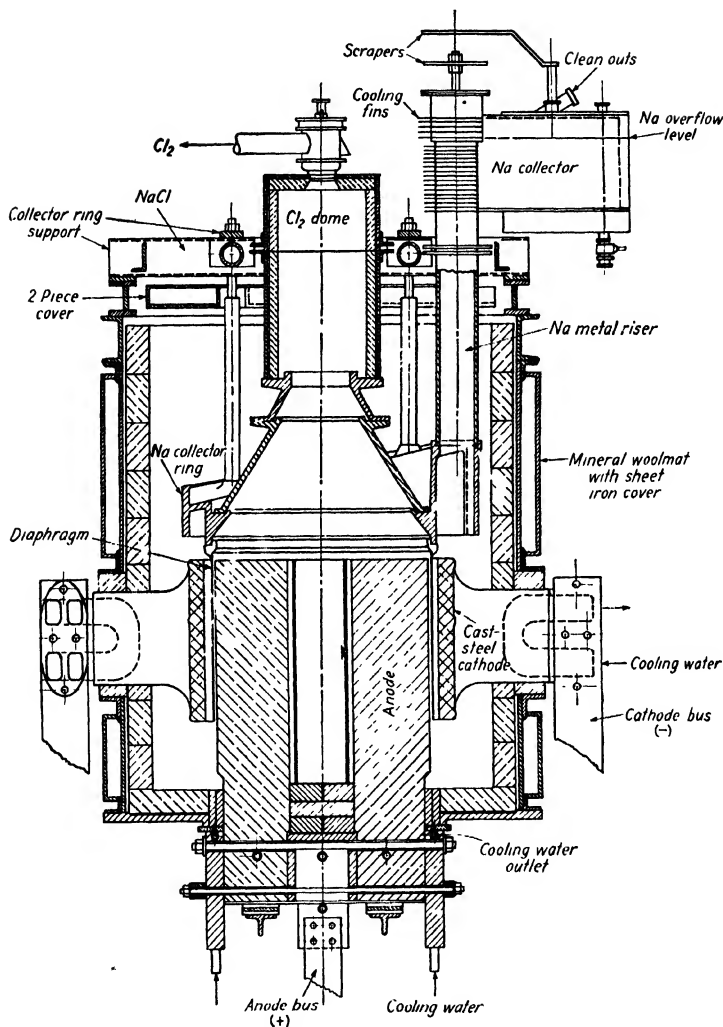
Fig. 189. Knapsack sodium cell.

of the cell. The electrolyte is 58 to 59 per cent $CaCl_2$ and 42 to 41 per cent NaCl and operates at 590 to 595°C.[42]

The sodium collected in the inverted trough rises in a vertical

[42] GARDINER, W. C., Tech. Industrial Intelligence Branch, U.S. Department of Commerce, *FIAT Final Rept.* 820 (PB 44,671), June 20, 1946.

TABLE 71. OPERATING DATA OF GERMAN SODIUM METAL PRODUCTION

	24,000-amp cell	32,000-amp cell
Electrolyte:		
$CaCl_2$, % .	58–59	58–59
NaCl, %. .	42–41	42–41
Production Na metal per day	385 kg (850 lb)	515 kg (1,130 lb)
Production Cl_2 per day	590 kg (1,300 lb)	790 kg (1,740 lb)
Current efficiency, av. %	78	
Voltage:		
Starting	5 7	
Final.	6 0	
Kwhr/lb Na..	5 2	
Kwhr/ton Na	10,400	
Lb Na per kwhr .	0 192	
Cells:		
Material of construction	Steel, acidproof, brick-lined	Steel, acidproof, brick-lined
Size steel shell, inside dimensions, diam. × depth	1,620 × 2,010 mm (63″ × 78″)	1,620 × 2,307 mm (63″ × 90″)
Brick lining, Durex II, thickness. . . .	105 mm (4.1 in.)	105 mm (4 1 in.)
Over-all height, busbar to Na collector. . . .	3,798 mm (148 in.)	4,345 mm (170 in.)
Temperature, °C .	585–595	
Life, anode life, days .	300–350	
Insulation in sheet iron cast	40 mm (1.6 in.)	40 mm (1.6 in.)
Temperature sodium collector, °C.	200–250	
Anodes:		
Material of construction	Graphite	Graphite
Size, length .	1,464 mm (57.6 in)	2,029 mm (80 in)
Cross section, each piece	254 × 254 mm (10″ × 10″)	410 × 410 mm (16″ × 16″)
Weight, approx.	1,200 kg (2,640 lb)	2,130 kg (4,686 lb)
Number	8	4
Life, days	300–350	
Sealing surface through shell, height. .	180 mm (7 in.)	322 mm (12.6 in.)
Cathodes:		
Material of construction	Cast steel	Cast steel
Size, outside diameter	995 mm (38.8 in.)	1,065 mm (41.5 in.)
Inside diameter	915 mm (35.7 in.)	966 mm (37.7 in.)
Height	864 mm (33.7 in.)	1,150 mm (44.9 in.)
C. d. cathode	9,700 amp/m² (902 amp/sq ft)	9,700 amp/m² (902 amp/sq ft)
Cathode leads, bus.	356 × 100 mm (13.9″ × 3.9″)	400 × 120 mm (15.6″ × 4.7″)
Cathode leads, over-all distance	2,260 mm (88 in.)	2,490 mm (97 in.)
Diaphragms:		
Material of construction. .	16-mesh iron and steel screen	16-mesh iron and steel screen
Size, outside diameter ...	876 mm (34.2 in.)	926 mm (36 in.)
Height	939 mm (36.6 in.)	1,208 mm (47.1 in.)
Life, days.	20–30	

pipe and overflows into a collecting pot which is drained every 2 hr into a small collecting car. The collecting car is drained into one of two electrically heated storage tanks maintained at about 120°C. When a storage tank is nearly full of sodium, it is closed and nitrogen at 1 to 2 atm is applied to force the sodium through a filter attached to the bottom of the tank. This filtration removes calcium which crystallizes out of solution as the sodium cools. The filtered sodium is cast into molds on a casting machine giving bricks weighing 4 kg (8.8 lb). The metallic calcium is scraped off the filter and removed to a heated hydraulic press to squeeze out most of the sodium. This calcium is then returned to an old cell which is running hot and specially equipped with a second pipe on the sodium collecting ring. In the cell the calcium is recovered by the following reaction:

$$Ca + 2NaCl = 2Na + CaCl_2$$

The assembled anode, cathode, and shell are set on the supporting steelwork on transite insulating pads. Water cooling lines are connected to both the anode and cathode contacts with short lengths of rubber hose in each line for electrical insulation. Busbars are bolted on.

The remaining parts are supported from two steel channels spanning the top of the cell. The two channels are fastened together by angles near each end by two 2-in. pipes spaced 340 mm (13.3 in.) each side of the center. Above the pipe flat pieces of steel 20 by 80 mm (0.8 by 3.1 in.) are welded to the upper flanges of the channel and extend outside the channels approximately 80 mm (3.1 in.). Four holes 35 mm (1.4 in.) in diameter are drilled in the protruding end of these steel pieces to accommodate the four supporting bolts for the sodium collector ring. These supporting bolts are 50 mm (2 in.) in diameter inside the cell and turned down and threaded with 1¼-in. bolt thread on the upper end. The diaphragm is made of 16-mesh steel screen and is accurately formed and assembled on a jig. There are steel stiffener rings fastened to the outside of the screen to help keep its shape. At the top, the screen is riveted to a cast-iron ring which is pinned to the collector ring. The three parts of the chlorine dome are grooved to fit on top of one another. The sodium collector and top part of the sodium-

collector riser are bolted to the flange of the sodium riser, coming out of the sodium collector ring.

The cell has two half covers that fit rather loosely around the necessary openings, which include the sodium riser, the chlorine dome, the four supporting bolts of the sodium collector ring and salt feed hole. The covers are sheet iron filled with 40 mm (1.6 in.) of rock wool insulation. The cell must be insulated from the ground to prevent current leakage.

Before a new cell is ready to start, the brickwork must be thoroughly dried out by a low charcoal fire for a week. The charcoal is burned in the space between the anode and the brick-work. The cell is started without the sodium collector ring, dia-phragm, etc., being in place. Four graphite wedges about 35 mm (1.4 in.) wide are placed 90 deg apart between the cathode and anode, and the cell is filled with broken electrolyte. Full cur-rent is put through the cell. The heat developed in the wedge melts the electrolyte. During this melting operation a hood is placed over the cell and connected to the vent suction line. When the cell is full of molten electrolyte at about 600°C, the graphite wedges are taken out, the hood is removed, and the remaining parts of the cell are installed and assembled. The chlorine line is connected to the dilute chlorine gas main because the gas is dilute for several days. Under normal operation the gas in the concentrated gas main should be 95 to 96 per cent Cl_2, the rest being air.

In starting a complete unit of cells, they are started one at a time, so the electrical equipment must be capable of going down to about 10 volts at full current.

The electrolyte level is maintained just below the top of the upper circle of bricks. Salt is added continuously and at such a rate as to maintain a constant level. The electrolyte is agitated with dry air where the salt enters. Every day 5 to 6 kg (11 to 13 lb) of dried $CaCl_2$ are added. Twice a week the electrolyte is analyzed and adjustments are made according to the analysis. The electrolyte composition is also checked and adjusted when changing the diaphragm. The electrolyte should contain 58 to 59 per cent $CaCl_2$. The $CaCl_2$ make-up is 90 per cent $CaCl_2$, 10 per cent $NaCl$, prepared by melting the mixture in an electric resistance furnace. Dry electrolyte is also prepared by melting

the proper mix in the same furnace. The amount of $CaCl_2$ required is 4 kg (8.8 lb) per 100 kg of Na metal.

The cell starts with a voltage of 5.7. As the graphite wears, the voltage goes up to 6.0 volts. The cell temperature starts at 585°C, with all the insulation in place. The cell life is 300 to 350 days. The diaphragm lasts only 20 days. It is necessary to change the diaphragm when the voltage suddenly rises to 8.5 to 9 volts.

Among the cells developed using liquid cathodes in the production of metallic sodium from NaCl, that of Acker had as its ultimate purpose the production of NaOH.[43] The furnace consisted of an irregularly shaped cast-iron box with slanting sides on which there was no machine work except that required on the terminal where connection was made with the copper bars which carried the current. The furnace casting was divided into three compartments, one of which was relatively large, was lined with magnesia or "magnesite" brick, contained the molten salt, and constituted the decomposing chamber. The bottom of this chamber (the "hearth" of the furnace) was covered with a shallow body of lead, usually about 1 in. deep, which also extended into the other chambers through connecting channels. This body of lead on the hearth was caused to move continually in one direction to one end of the decomposing chamber, where it passed through a short channel into one of the small chambers called the "well." From here it was elevated and forced over a dividing wall or partition into the adjoining small chamber or caustic chamber, from which the lead passed into and through a long channel to the other end of the furnace casting, where it again spread over the hearth and came in contact with the salt.

In starting a furnace molten lead was first poured over the hearth to the requisite depth. Two of the anodes were placed in position, but these anodes were equipped for starting purposes with a number of small carbon rods or "pins" about 1 in. in diameter and 5 in. long, which were fitted into the lower end of the anode proper and from which they extended into the lead. When these anodes were in position, the salt was shoveled into the furnace until they were entirely surrounded and covered up, after which the furnace was cut in in series with all the other

[43] ACKER, C. E., *Trans. Am. Electrochem. Soc.*, **1**, 169 (1902).

furnaces. The full current passed down the starting anodes and through the small carbons. These soon became red hot and later almost white hot, causing the surrounding salt to melt and the entire furnace and contents to come up gradually to the working temperature. The rapidity with which the furnace was brought up to the desired temperature was regulated by the number of carbons or pins attached to the lower end of the regular working anodes. Furnaces were started on 4 volts and, if cold, continued at 4 volts for some time.

A current of 8,000 amp was employed in one series of furnaces with 4 anodes to a furnace. Each anode therefore conducted a current of 2,000 amp which fused the salt, maintained the temperature at a low red heat, and decomposed it, the current density being 2,750 amp per sq ft (295 amp per dm²). The average current efficiency was 93 per cent, higher values being claimed on individual furnaces.

BERYLLIUM

Metallic beryllium was discovered at about the same time as aluminum and magnesium, in 1828. Wöhler obtained the metal through the reduction of its chloride with metallic potassium. Because of the difficulties encountered in its production, beryllium has been disregarded for nearly a century. It was not until 1921 that Stock, Goldschmidt, and Praetorius in Germany succeeded in producing the metal in a compact form by electrolyzing its molten salts.

The properties of beryllium have aroused the interest of many investigators. It is the lightest known inert metal, being about two-thirds as heavy as aluminum, but little more than magnesium, and less than twice as heavy as water. Relative volumes of equal weights of beryllium and steel are shown in Fig. 190. Unlike magnesium and aluminum, it is one of the hardest metals, readily scratching glass. On variation of temperature it expands and contracts in a manner similar to iron. It may be highly polished, remaining untarnished in air. It is only slightly attacked by influences which readily affect aluminum and magnesium. It is gray in color, closely resembling steel, with a melting point of 1285°C. It may be heated to 600°C without marked effect.

Ores and Extraction Processes. Beryllium is found in at least 15 minerals, varying from almost pure BeO to complex silicates containing very small quantities of the element. Practically the only recognized source is beryl, a hard, stony, opaque substance containing 12 to 15 per cent of BeO, 19 to 22 per cent of Al_2O_3, and approximately 67 per cent of SiO_2. Such an ore will therefore contain only 4 to 5 per cent of metallic beryllium, since the metal represents about 36 per cent of the oxide. Even with pure beryllium compounds, the working out of a suitable process for the extraction of beryllium is difficult. The application of aluminum technology is of little value. Aluminum, melting at 657 to 660°C, can be readily electrolyzed out in a molten condition; but the high temperature required to melt beryllium (1285°C) involves complex problems.

FIG. 190. Relative volumes of equal weights of beryllium and steel. (*Beryllium Corporation of America.*)

In the method developed by the Beryllium Corporation of America, molten metal is not produced directly in the electrolysis furnace, as in the case of aluminum and magnesium; but the product is obtained in flake form, which is separated from the electrolyte, washed, dried, subjected to mechanical pressure and further furnace treatment to cause coalescence into ingot form.

Cooper[44] states that

. . . of all the work on ore processes, only the method indicated by Copaux[45] had merit enough to warrant further consideration for commercial scale operation. The process consists in heating ground beryl with several parts of sodium silicofluoride to approximately 850°C. Decomposition takes place, with the formation of the sodium double fluorides of aluminum and beryllium. The beryllium salt is quite

[44] COOPER, H. S., "Beryllium, the Light Metal of the Future," Cleveland, 1927.

[45] COPAUX, H., *Compt. rend.*, **168**, 610–612 (1919).

soluble in water, while that of aluminum is insoluble. Effective separation is obtained by leaching.

The process of the Brush Beryllium Co.[46] consists in converting the metal oxides in beryl into sulfates, separating pure beryllium sulfate by crystallization, and decomposing the beryllium sulfate by heat into sulfur oxides and beryllium oxide. The crude beryl is crushed in a gyratory, the crushed ore melted and quenched in cold water. The chemically resistant natural beryl crystals are converted into a reactive glass. After drying, the brittle beryl glass is ground in a pebble mill to pass a Tyler 200-mesh sieve. The ground beryl is then thoroughly mixed with 60 to 63°Bé sulfuric acid, with 5 to 10 per cent excess acid. The initial reaction is quite vigorous, and sufficient heat is developed to bring the mixture to boiling. The reaction is completed by maintaining the temperature at about 250 to 300°C until a dry material of sulfated ore is obtained. The soluble sulfates in the sulfated ore are leached out with water. In order to separate the aluminum from the beryllium, ammonium sulfate is added to the clear filtrate and ammonium aluminum sulfate separated by crystallization. From purified mother liquors pure beryllium sulfate is crystallized after concentration and cooling. The pure beryllium sulfate is heated to 1000 to 1400°C to decompose the sulfate to beryllium oxide.

Beryllium is hard and brittle, resembling silicon in this respect. No thin sheet, wire, or ribbon has been made from it to date, as it is neither malleable nor ductile.[47]

Electrolysis. Chloride Process. According to the American process, beryllium is made as follows: The anhydrous chloride is best prepared by heating BeO with carbon in an atmosphere of chlorine, with CCl_4 and chlorine, or with phosgene. The $BeCl_2$ sublimes into the colder portion of the chlorination chamber, moisture and air being rigidly excluded. The chloride is then electrolyzed in a metal pot, preferably of a chromium-iron alloy containing about 20 per cent chromium and the balance iron. The corrosion resistance of such alloys prevents the introduction of iron into the flake metal deposited, either directly or by first

---

[46] U.S. Patents 2,018,473 and Reissue 20,214 issued to Charles B. Sawyer and Bengt Kjellgren include the above-described process.

[47] VIVIAN, A. C., *Trans. Faraday Soc.*, **22**, 211 (1926).

being dissolved as a salt in the molten bath and subsequently electrolyzed out in metallic form.

Five kilograms of $BeCl_2$ must be electrolyzed to obtain 500 g of metal. The bath may be a neutral halide or mixture of halides of a metal or metals more electropositive than beryllium, chlorides and fluorides being preferred. Since the available chlorides are more soluble than the fluorides, any solidified electrolyte clinging to the deposited metal is more easily separated when
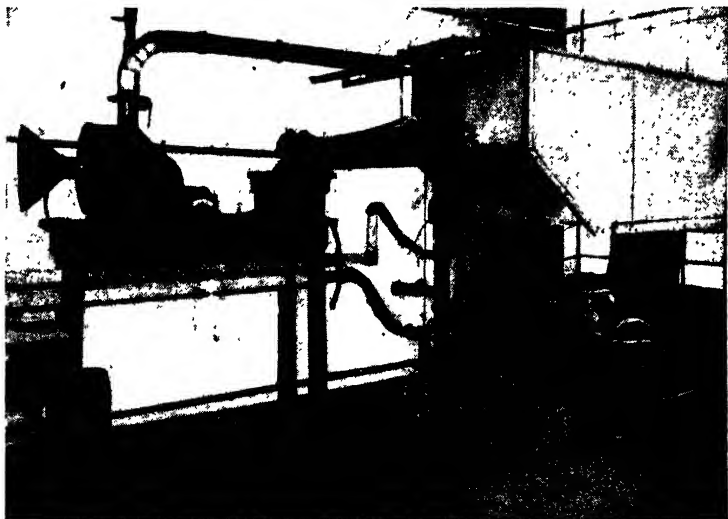
Fig. 191.   Beryllium electrolysis furnace.   (*Beryllium Corporation of America.*)

chlorides are used. As an example, 25 kg of NaCl may be used with 5 kg of $BeCl_2$. The metal pot, which acts as cathode, should be just large enough to hold this electrolyte and a graphite or carbon anode. It has been found preferable to use inert gases, such as hydrogen, to eliminate the danger of atmospheric oxidation. A typical furnace is shown in Fig. 191. One arrangement employs a dome-shaped cover provided with a small opening for the introduction of the inert gas during electrolysis and a larger hole for removing gases formed during the operation, such as chlorine and hydrogen, and for feeding in the anhydrous $BeCl_2$. The anode passes through a hole in the center of the

dome, fitted tightly by means of an asbestos ring which also serves as insulator.

Before the $BeCl_2$ has been added, the pot containing NaCl is heated until the salt begins to melt. Hydrogen is then introduced and the $BeCl_2$ slowly added. The temperature is maintained at about 730°C. As the $BeCl_2$ content of the bath is depleted, the temperature is raised, reaching about 820°C at the end of the run. An alternative method adds the $BeCl_2$ in small portions throughout the electrolysis, the temperature being held at about 800° during the run. The chief objection here is that lower current density must be employed to prevent anode effect.

Electrolysis is begun with about 600 amp, the voltage varying from 5 to 8 volts depending upon external resistances, contacts, and the like. Toward the end of the run the amperage is tapered off. At the conclusion of electrolysis the beryllium is found clinging to the inner wall of the pot, together with fused salt. The mass is scraped out into iron pots, a thin coating of salt protecting it from oxidation. When cold, the material is broken up and the salt leached rapidly from the metal with cold water. The metal is then washed with alcohol and dried. It is in the form of large, bright crystalline plates and spangles, quite free from oxide and other impurities.

If heated in this divided condition, the metal oxidizes rapidly and will neither form a regulus nor alloy with other metals present. To bring it into coherent form, it is pressed in steel dies under several tons pressure into strong rods, disks, and the like. These are heated to 1300 to 1450°C in a closed crucible with a fused salt, such as $BaCl_2$ or a 90 per cent $BaCl_2$ 10 per cent BaF_2 mix. The particles coalesce, forming a coherent ingot or regulus of bright metal. A complete fusion of the metallic contents of the crucible is obtained in this manner. The presence of 10 per cent fluoride in the flux facilitates the fusion of metal, since the fluoride tends to dissolve the thin film of oxide to which beryllium owes its stability in air, thus making coalescence possible.

Electrolysis. Fluoride Process. Illig[48] described the Siemens-Halske method for the production of beryllium, based on the use of the double fluorides of beryllium and sodium as electrolyte. The development of beryllium manufacture was accomplished

[48] ILLIG, K., *Trans. Am. Electrochem. Soc.*, **54**, 53 (1928).

by Stock and Goldschmidt with the cooperation of Priess and Praetorius, who obtained metallic beryllium in the form of large reguli directly from a fused electrolyte. . Earlier work had failed because, at the instant the metal was formed, it was at once reoxidized or vaporized. Salts previously used as electrolytes evaporated before the real reduction started, or the viscosity of the fused salt was too high, or finally, the affinity between the anion and cation was too great to allow separation under the conditions existing at that time.

Stock and Goldschmidt attempted to find a method in which all the restricting conditions would be eliminated They felt that the electrolytic separation of beryllium from a fused salt mixture could be possible only if a salt were used which, at the required temperature, did not evaporate at all or did so only slightly. On the other hand, to avoid an unusually high potential drop between the electrodes, the salt must also possess a very low viscosity at the melting point of beryllium, 1285°C. The anions must be easily separated or removed from the electrolyte. Thus the separated metal might be prevented from remaining in, or being redistributed in, the surrounding fused salt mass.

These conditions were fulfilled in general by the double fluorides of beryllium with sodium and barium. The barium-beryllium fluoride has an appreciable viscosity around 1300°C, but also has the advantage of being only slightly volatile at this temperature range. It has an appreciable dissociation within this range. The sodium-beryllium fluoride is strongly dissociated even at relatively low temperatures, giving an electrolyte of good conductivity. It has the disadvantage, however, that at very high temperatures the separated beryllium metal may be volatilized in appreciable quantities.

If the electrolysis be started with the sodium-beryllium fluoride and some barium-beryllium fluoride be added in increasing amounts with rising temperatures, a useful mixture of the double salts is obtained for every temperature interval. When the final metal separating temperature of 1300 to 1350°C is reached, it is not difficult to continue the electrolysis for many hours, provided suitable additions of both salts be made from time to time.

Graphite containing as little iron as possible is the only material to use for the crucible which serves as anode. Some difficulties

were encountered in mounting the electrodes of the crucible. The most satisfactory cathode material was a special iron made up into a hollow, water-cooled form.

The electrolyzing current is sufficient to maintain the bath at the required temperature. The crucible is first filled with pieces of carbon or graphite, the iron cathode being pressed firmly against these pieces. As soon as the proper temperature is reached, the pieces are quickly dumped out of the crucible and a charge of low-melting sodium-beryllium fluoride is immediately put in. Then barium-beryllium fluoride is added until the required temperature range is reached for the electrolysis to begin.

In the older methods the electrolyte became more and more enriched in BaF_2, thus shortening the time of a single charge. With the use of new salts, however (stated to be beryllium oxyfluoride plus BaF_2), it is possible to make the process continuous, limited only by the burning of the graphite crucible. Fluorine liberated during the process attacks the anode, forming carbon oxyfluoride, which in turn, by interaction with oxygen, forms CO in large amounts.

Sublimation products formed during electrolysis are recovered, reprecipitated, and reused, poisonous gases such as fluorine and CO being drawn off. Material yields of approximately 95 per cent and current yields of about 80 per cent are claimed to be not uncommon. The beryllium metal reguli vary with the size of equipment, being ordinarily in the neighborhood of 150 g. The metal is about 98 per cent pure, which value can be raised by special treatment and at a sacrifice of yield to 99.9 per cent. Iron from the graphite crucible constitutes the chief impurity.

The double decomposition methods of the raw beryl for the formation of the electrolyte salts produce about 65 per cent of beryllium, calculated as metal. Hence the final yield is approximately 60 per cent.

Beryllium imparts heat-treating characteristics to copper, nickel, cobalt, and iron. It does not alloy with magnesium, and its aluminum alloys lack ductility to enable them to be rolled.[49] There has been no commercial use of beryllium in the light-alloy field, but there has been considerable application as low percentage beryllium (0.5 to 2.5 per cent) copper and nickel

[49] STOTT, L. L., *Iron Age*, **144**, 42 (1939).

heat-treatable materials. For these uses the metal is prepared as an alloy from BeO, carbon, and a metal such as copper by reaction above 1600°C in a manner similar to the procedure for
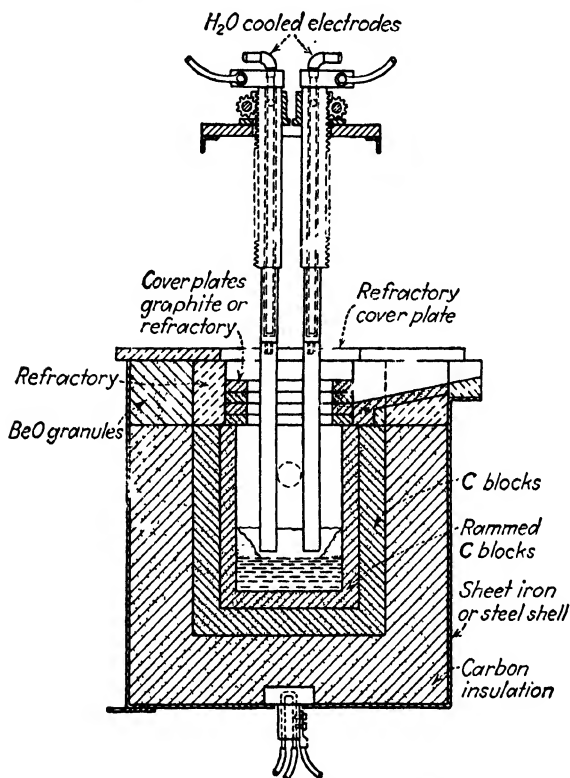
FIG. 192. Arc furnace for the production of beryllium alloys.

aluminum-copper alloys from Al_2O_3, carbon, and copper in an arc furnace.

The beryllium alloys are produced in an arc furnace as shown diagrammatically in Fig. 192.[50] The furnace consists of a steel shell with carbon insulation surrounding a shell of carbon blocks, which in turn enclose a crucible made of rammed baked carbon. Vertical adjustable water-cooled graphite electrodes with a third bottom electrode are employed. The furnace is mounted on trunnions and discharges through a lip. The charge to the

[50] British Patent 500,469 (Feb. 6, 1939).

furnace consists of the heavy metal (copper or nickel), BeO, and carbon, which mixture has been ground in a ball mill. Small amounts of charge are introduced, the electrodes lowered, and arcs struck. The furnace is gradually filled up and the electrodes slowly raised, while arcs for heating are maintained. The BeO at the operating temperature of 1800 to 1900°C is reduced by carbon to form metal and CO, the heavy metal, in liquid form, alloying with the beryllium. Under steady conditions there is a layer of molten metal at the bottom of the furnace and charge floating on this. The charge contains small particles of heavy metal which melt and pass down through the unmelted charge. Melting beryllium and its vapors alloy with the molten heavy metal and the mixture falls down to the main body of metal at the bottom of the furnace. Tapping is intermittent. Operating data are given in Table 72.

TABLE 72. ELECTROLYTIC PRODUCTION OF BERYLLIUM ALLOYS

Typical furnace charge:	
Copper, %......	82
Beryllium oxide, %	12
Carbon, %........	6–6 5
Form of furnace charge.......	Powder or loose mixture
Furnace size................	10 in. diameter
Furnace voltage..........	38
Furnace current, amp........ ...	600
Operating temperature, °C.... ...	1800–1900
Be content of alloy, %.............	4–5
Be yield from oxide, %.	78
Power requirements, kwhr/lb Be in alloy	55

CALCIUM

Calcium is manufactured by the electrolysis of the fused chloride.

It is difficult to prepare pure anhydrous $CaCl_2$ owing to hydrolysis. In the presence of impurities, calcium metal is attacked by the melt. The bath thickens, the conductivity decreases, and the yield of calcium falls. Metallic calcium to the extent of 17 per cent can be taken up by the melt, together with several per cent of iron (assuming an iron container); the condition of the electrolyte grows worse with each cooling and reheating. In commercial work the electrolyte must occasionally be completely changed. Calcium oxide is soluble to the

extent of several per cent in fused $CaCl_2$. When electrolyzed, the oxide content is reduced to zero. Basic salts of a lower oxide of magnesium, CaC_2, and carbon, all build up in the electrolyte as impurities which necessitate electrolyte change.

Pure $CaCl_2$ melts at 780° and impure calcium metal at 800°C. The finely divided metal burns in air above 800° and easily forms metal fog in the electrolyte. The range of safe working temperatures is small.

Arndt and Willner[51] state the decomposition voltage of $CaCl_2$ at 800° to be 3.24 volts. Arndt and Gessler[52] give the specific conductivity of the salt at 800° as 1.9.

Ruff and Plato[53] made small quantities of calcium metal using an electrolyte of 100 parts $CaCl_2$ and 16.5 parts CaF_2, melting at 660°. The bath temperature was 760° and was raised to 800° in the immediate neighborhood of the cathode, as the result of high cathodic current density (3 to 5 amp per mm² or about 1,900 to 3,200 amp per sq in.) at 30 volts.

A number of laboratory studies of calcium production have been made.[54] The commercial method for calcium production uses a vertical contact cathode, upon which the calcium is deposited as the cathode is continuously moved upward. The operating details are given in Table 73.

In reference to the energy consumption figure in Table 73, the variation between 30,000 and 50,000 kwhr per ton is a function of (1) the size of the furnaces employed, (2) the details of construction and carefulness of insulation of these furnaces, and (3) the length of the operating campaign before changes need to be made either in the electrolyte, in the cell proper, or in the electrical connections. The lower figure is obtainable with large cells and long campaigns, while the higher figure is encountered in connection with small cells either infrequently operated or

---

[51] ARNDT, K., and WILLNER, K., *Z. Elektrochem.*, **14**, 216 (1908).

[52] ARNDT, K., and GESSLER, A., *Z. Elektrochem.*, **14**, 662 (1908).

[53] RUFF, O., and PLATO, W., *Ber.*, **35**, 3612 (1902).

[54] WÖHLER, F., *Z. Elektrochem.*, **11**, 612 (1905); BRACE, P. H., *Trans. Am. Electrochem. Soc.*, **37**, 465 (1920); *Chem. & Met. Eng.*, **25**, 105 (1921); GOODWIN, J. H., *J. Am. Chem. Soc.*, **25**, 873 (1903); **26**, 1403 (1904); JOHNSON, A. R., *Trans. Am. Electrochem. Soc.*, **18**, 125 (1910); FRARY, F. C., BICKNELL, H. R., and TRONSON, C. A., *ibid.*, **18**, 117 (1910); RATHENAU, W., *Z. Elektrochem.*, **10**, 508 (1904).

producing calcium metal for only short periods. Figure 193 shows an early commercial cell for the manufacture of calcium.
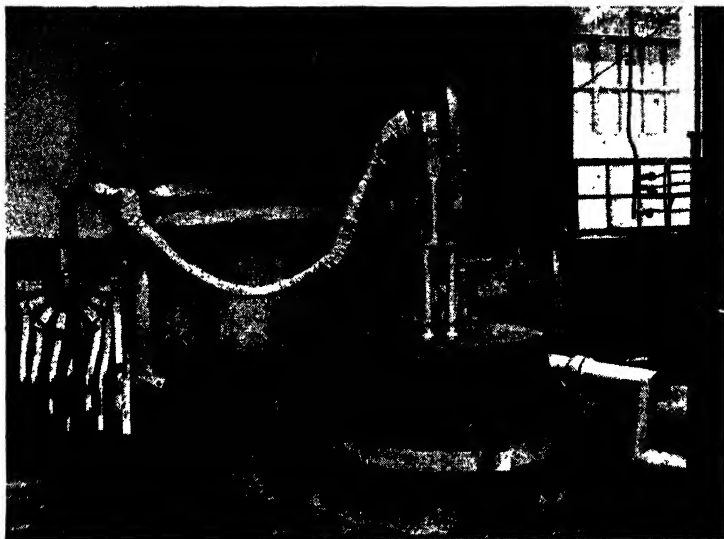
FIG. 193. Commercial calcium cell. (*Société d'Electrochimie et d'Electrométallurgie d'Ugine, Jarrie, France.*)

TABLE 73. OPERATING DETAILS FOR THE ELECTROLYTIC PRODUCTION OF CALCIUM

Electrolyte..............	Pure calcium chloride
Temperature, °C.......	. 780–800
Current:	
C.d., amp/sq in. cathode..	650 (100 amp/cm^2)
Energy consumption.............	30,000 to 50,000 kwhr/ton, (15–25 kwhr/lb)
Theoretical decomposition voltage of	
CaCl$_2$ at 800°C.....	3 220
Melting point of CaCl$_2$, °C	780
Specific conductivity of CaCl$_2$ at 800°C	1 921
Lb CaCl$_2$ per lb Ca (theoretical).... .	2.76
Lb CaCl$_2$ per lb Ca (actual)..........	4.5
Anodes...........................	Graphite
Cathodes:	·
Material.......................	Iron or graphite coated with calcium
Type...........................	Vertical, with surface contact
Cells:	
Lining.........................	Carbon
Casing.............	Sheet steel

Low recovery values of $CaCl_2$ in terms of calcium metal are chiefly due to the atomizing effect of the violent chlorine evolution. This causes a fine spray of electrolyte which is carried up the flue of the ventilating system. Other losses are due to the necessary skimming of the bath at intervals and to the layer of chloride formed on the calcium as it is drawn from the bath. Once in operation, the cathode is effectively one of calcium metal. Thin layers of $CaCl_2$ protect the metal from the air. The commercial metal may contain small quantities of carbon, carbide, and alkali and alkaline earth metals.

German practice is reported as 25 volts per cell, with currents of 1,400 amp, requiring 36 kwhr per lb of metal from cells producing 13 kg per cell per day (28.6 lb).[55]

CERIUM

The electrolytic production of cerium in appreciable quantity was first accomplished by Muthmann, Hofer, and Weiss[56] from a melt of 90 per cent $CeCl_3$ and 10 per cent KCl and NaCl. A copper crucible, with the upper half water-jacketed, formed the cell. The cathode and anode were carbon rods, the one inserted in the bottom of the crucible, the other suspended above it. Voltages were of the order of 12 to 15 volts. Developments by Hirsch[57] offered a simpler process. His cell was a short piece of 3-in. iron pipe screwed at one end into a 5-in. iron flange on which a well-faced iron plate was bolted to form the bottom of the cell, the entire arrangement serving as cathode. The anode was a small graphite rod. A small quantity of NaCl was first fused in the cell; then $CeCl_3$ was added until good conduction was established. A little KF and $BaCl_2$, added from time to time, respectively eliminated any oxide formation and increased the resistance and temperature of the melt. Current efficiencies were of the order of 36.5 to 41.5 per cent, with voltages of 12 to 14 volts and currents of 200 amp. In technical practice, cells were cast-iron pots 8 in. in diameter and 18 in. deep, with anodic

[55] *PB Rept.* 49,025, Office of Technical Services, U.S. Department of Commerce.

[56] MUTHMANN, W., HOFER, H., and WEISS, L., *Lieb. Ann.*, **320**, 231 (1902).

[57] HIRSCH, A., *Trans. Am. Electrochem. Soc.*, **20**, 57 (1911); *Chem. & Met. Eng.*, **19**, 511 (1918).

current density of 5.5 to 6.5 amp per sq in. (85 to 100 amp per dm²), depending upon whether carbon or graphite anodes were used. Cathodic current densities were one-third to one-quarter the value at the anode. At the end of 24 hr, alkaline chloride had piled up in the bath to so great an extent that electrolysis was discontinued. Stirring just before the end of the run caused the metallic particles to aggregate together.

To prevent the formation of drops of cerium throughout the electrolyte and a consequent loss of metal, anhydrous $CeCl_3$ must be used and the alkaline chloride content of the melt must be kept low. Careful temperature regulation is essential so that, on the one hand, metal fog production and the alloying of cerium with iron at high temperatures may be avoided, and on the other, metallic conductance rather than electrolysis may not occur.

Cerium is used as a constituent of Misch metal, an alloy of cerium with other metals of the same group. The Misch metal is used in the manufacture of pyrophoric alloys (65 to 70 per cent cerium metals and 30 to 35 per cent iron) from which "flint" lighters, automatic gas lighters, and tracer bullets and shells are made. It is electrolytically produced from fused chlorides which result from the treatment of residues of monazite sand from which the thoria have been removed.

COLUMBIUM

Metallic columbium was made by the electrolysis of fused potassium columbium oxyfluoride. No oxide addition was necessary to prevent an anode effect. Graphite was used as the anode and a cast-iron pot as the cathode. Balke[58] states that after much experimentation with various additions to the bath, with temperature of operation, current density, etc., electrolytic columbium powder was finally obtained. However, in relation to the large quantity of salt handled and the time and power consumed in making the runs, the yield of metal was very unsatisfactory.

The electrolytic method was replaced by a process in which a mixture of columbium carbide and oxide is heated in a vacuum with the liberation of carbon monoxide and the formation of columbium metal.

[58] BALKE, C. W., *Trans. Electrochem. Soc.*, **85**, 89–95 (1944).

Top view

Cl$_2$ outlet   LiCl feed ports   Insulation

Graphite anode shafts

75

150

A ———— A

Graphite anode plates

50

75

Refractory plates

450
550
600
750

All dimensions are in millimeters

Section A-A

350
250
100
25

Steel cover plates

Rim for diaphragm support 200 mm φ

Steel shell

50

200

Cast iron lithium collector head 10 mm thick

Wire screen

50

55

Steel cathode head 102 mm φ & 125 mm high

70

70

Steel shaft 50 mm φ

Graphite plate anode

160

685

50

50 mm thick refractory plates

Steel collar

300

Insulation 100 mm thick

Fig. 194. Lithium electrolytic cell.   Design of Degussa, Rheinfelder, Germany.

LITHIUM

Lithium is an alkali metal although in some respects it has properties similar to calcium and magnesium. Lithium is very reactive chemically, rapidly absorbing oxygen and nitrogen from the air to form oxides and nitrides. It is best known in the form of its salts and its hydride. Its ores are available in considerable quantities as spodumene, a lithium-aluminum silicate containing about 3.8 per cent lithium; lepidolite, a lithium mica containing 0.8 to 2.7 per cent lithium; triphyline, a complex double phosphate containing sodium, iron, and manganese and about 3.6 per cent lithium; and other minor ores.

The lithium values in these ores are concentrated by wet chemical processes in which the lithium is recovered as a carbonate. The metal can be produced by electrolysis of fused halides of potassium and lithium. The electrolytes used are either LiCl and KCl or these with some LiBr.

Commercial cells produced lithium metal from LiCl at a current efficiency of over 90 per cent and a metal yield, on the basis of the LiCl input, of 95 per cent. The lithium metal was 99.5 per cent pure and was produced in the same type of cell as employed for the electrolytic production of sodium metal.[59]

Operating details of a German plant are given in Table 74, while the cell is shown in Fig. 194.

Purity of the electrolyte and the cell feed is quite important. Sulfates, SiO_2, Ba, Ca, and Fe_2O_3, lower the current efficiency and the cell output. The cell is filled with molten electrolyte upon the starting of operations. Lithium is ladled out of the top section of the collecting head where it is protected by a layer of petroleum oil of high boiling point.

LEAD ALLOYS

Alloys of lead containing barium and calcium were produced by the electrolysis of fused salts in which fused chlorides of barium and calcium were electrolyzed over a bath of molten lead as a cathode. Calcium-barium-lead alloys are described in the patent literature.[60]

[59] Osborg, H., *Trans. Electrochem. Soc.*, **66**, 91 (1934).

[60] deCampi, E. A., U.S. Patent 1,360,272; Wettstein, T. F., U.S. Patent 1,360,339; Worrall, G. H., U.S. Patent 1,360,348; Mantell, C. L., "Indus-

TABLE 74. ELECTROLYTIC PRODUCTION OF LITHIUM

Lithium:
Sp gr........	0.534
Melting point, °C... .	186
Raw material.........	LiCl (94–98% LiCl, 2.5% KCl, 1.5% NaCl, 0.5% Fe_2O_3)

Electrolyte:
Per cent LiCl........	52
Per cent KCl..	48
Temperature, °C.	400–420

Cell:
Material of construction... ..	Firebrick box with dense refractory brick lining
Diaphragm.................	24-mesh iron wire
Shape.....................	Square
Size......................	17.7″ × 17.7″ × 19.1″ (450 × 450 × 485 mm)
Electrolyte capacity.........	220 lb (100 kg)

Current:
Amp per cell...	850–900
Voltage across cell...	8–9
Current efficiency, %.... ..	85–90
Amount of Li per 1 000 amp-hr	0.485–0.53 lb (220–240 g)

Anode:
Material..................	Graphite
Size.................... ...	5.9″ × 23.6″ × 2.8″ (150 × 600 × 70 mm)
Number....................	3
Active anode area...........	89.28 sq in. (576 cm^2)
Anode c.d................	1,300.6 amp/sq ft (1.4 amp/cm^2)

Cathode:
Material...................	Steel
Size.....	4″ diam × 4.92″ high (102 × 125 mm)
Number.........	1
Active cathode area....	62 sq in. (400 cm^2)
Cathode c.d....... ...	1,950.9 amp/sq ft (2.1 amp/cm^2)

Li production per cell per day...	8.8–11 lb (4–5 kg)
Power, d.c. per lb of Li, kwhr ..	140
LiCl per lb Li. .. .	16.06 lb (7.3 kg)
HCl required per lb Li.... .. .	0.66 lb (0.3 kg)

Analysis of product:
Li, %..	97
K, %...	1.3
Na, %........	1.4

trial Electrochemistry," 2d ed., p. 448, McGraw-Hill Book Company, Inc., New York, 1940; MANTELL, C. L., and HARDY, C., "Calcium Metallurgy and Technology," Reinhold Publishing Corporation, New York, 1945.

ZIRCONIUM

Zirconium metal has been made through the steps of reacting zirconium oxide with carbon to form low silicon zirconium carbide or crude zirconium metal in an electric-arc furnace, the conversion of this carbide to a dense low-oxide chloride, and the reduction of this chloride with magnesium to produce zirconium metal. This metal is melted in a carbon resistor furnace to produce zirconium shapes for fabrication.[61]

[61] KROLL, W. J., SCHLECHTEN, A. W., CARMODY, W. R., YERKES, L. A., HOLMES, H. P., and GILBERT, II. L., *Trans. Electrochem. Soc.*, **92**, 99–113 (1947).

Part IV
ELECTROTHERMICS

CHAPTER 20

ELECTROTHERMICS IN GENERAL

The usefulness of electric furnaces and electric heating in chemical and metallurgical work was demonstrated long before there was a sufficient supply of electric power for the commercial development of possible applications. Davy produced sodium and potassium in an apparatus that was really a small electric furnace. In 1839 Robert Hare[1] operated an electric furnace in a vacuum under a bell jar by means of a battery current and produced CaC_2, graphite, phosphorus, and calcium.

The manufacture of many electrochemical and electrometallurgical products requires temperatures higher than those obtainable by combustion methods. In this particular field there is no competition with heating obtainable by the use of fuels. In general, electric heating shows greater flexibility of application than do competitive methods of gas or solid fuel combustion. Electric heat can usually be developed at, or adjacent to, the point of use more rapidly than fuel heat. In electric heating there is a lower temperature gradient between the heat source and the point of use. In contradistinction, flame temperatures are often 500 to 1100°C higher than the working temperatures required. Smoke, grease, dirt, ashes, moisture, fumes, and other products of combustion are eliminated. Ordinarily less time and attention in operating and maintaining the apparatus are needed. In general, electric heating tends toward more comfortable, convenient, and healthful living or working conditions. No air is required to support combustion and hence there are no thermal losses involved in preheating the air. Cumbersome and bulky combustion chambers and muffles are eliminated, with more efficient heat transfer as a result of these factors. No heat is lost through stacks except in certain types of low-temperature apparatus where moisture and volatiles have to be removed by ventilation. Electrical apparatus lends itself to careful and

[1] DOREMUS, C. A., *Trans. Am. Electrochem. Soc.*, **13**, 347 (1908).

TABLE 75. METHODS OF ELECTRIC HEATING

I. Resistance heating
    A. Substance heated functioning as resistor
        1. Solids as resistor
            a. Metal rods, rivets, etc., as resistor
            b. Carbon or graphite resistors (furnaces for producing graphite electrodes)
            c. Reactive furnace charges (electrothermic zinc)
        2. Liquids as resistor
            a. Water (instantaneous water heating, water rheostat)
            b. Fused electrolytes
    B. Auxiliary elements acting as resistor
        1. Metallic wire or ribbon resistors (usually nickel-chromium alloys, also molybdenum and platinum)
        2. Cast metallic resistors
        3. Nonmetallic resistors
            a. Silicon carbide compounds in form of rods and tubes ("Globar" elements)
            b. Granular carbon resistors (Baily furnaces)
            c. Carbon plate resistors under pressure
            d. Carbon core resistors, surrounded by charge (SiC furnaces)

II. Arc heating
    A. Direct-arc method
        1. Between electrode and substance
            a. Direct series arc (Heroult furnaces)
            b. Direct arc, free hearth electrode (Girod furnace)
            c. Direct arc, buried hearth electrode (Greaves-Etchells furnace)
            d. Mixed types of *a*, *b*, and *c* (Booth, Nathusius furnaces)
    B. Indirect-arc method
        1. Between two or more electrodes placed end to end (Detroit furnace)
        2. Between two or more electrodes mounted at angles to each other (Stassano, Rennerfelt furnaces)

III. Induction heating
    A. Low-frequency, core type
        1. Solid resistor as secondary (Kjellin furnace)
        2. Molten metal as secondary (Ajax-Wyatt, Ajax-Tama, Röchling-Rodenhauser furnaces)
    B. High-frequency, coreless type
        1. Combinations of conducting or nonconducting crucible and conducting or nonconducting charge (Ajax-Northrup furnace)

thorough insulating with a resultant reduction of radiation losses. Electric heating apparatus shows higher relative efficiency than fuel-burning equipment.

From the electrochemical viewpoint, perhaps the most important reason for the application of electric heating is that it allows higher temperatures to be obtained and processes to be simplified. At the higher temperatures obtainable in electric furnaces, many chemical reactions proceed which cannot be made to take place at lower temperatures with any appreciable speed. In many cases electric heating methods are the only ones available for the production of certain materials. Electric heating methods may be classified as in Table 75. The entire field will be divided into resistance, arc, and induction heating, the last being subdivided into low- and high-frequency applications.

From the electrochemical viewpoint, Secs. II and III are of considerably greater interest than is the larger part of Sec. I, with the exception of IA-2b, which has been discussed previously under fused electrolytes. The field of application of electric furnaces will be subdivided into (1) those employed for iron and steel, (2) those especially adapted to the melting of nonferrous metals and alloys, and (3) those commonly employed in the production of the ferroalloys. To this must be added (4) the discussion of nonmetallic products, such as CaC_2, SiC, graphite, as well as distillation products such as CS_2, produced in electric furnaces of the arc and resistance types.

In the method of heating by direct resistance, the heat necessary to keep the bath molten is produced by making use of the electrical resistance of the material being heated. Since heating is effected by the passage of the current through the liquid material, the heat is distributed throughout the mass. Inasmuch as the heat generated, I^2R, is proportional to the square of the current, the amount of heat could be regulated by changing the resistance of the furnace, and low-voltage currents could be used. In iron and steel metallurgy, however, the disadvantages outweigh the advantages, in that the specific resistance of iron is low. The high temperatures for melting could be obtained only by the use of very heavy currents requiring large investments in copper electrical connections. It might be possible to get around this by increasing the length of the bath and decreasing the cross section. Such an arrangement is not feasible because the large

area of bath resulting would entail disproportionate radiation losses and preclude the easy handling of slags and metal.

In indirect resistance heating, instead of depending upon the resistance of the material to furnish the heat required, some other conductor having a high resistance is built into the furnace in such a way that the heat generated in it would be absorbed by the material to be heated. This is the principle employed in furnaces of the SiC plate resistor and general resistance type. The method is not readily applicable to steel metallurgy, in that the resistor cannot be composed of carbon, which would be taken up by the steel. Any other type of resistor which might be used could not be placed in the bath because it would then be in an electrical circuit in parallel to the metal. The metal, being of lower resistance, would carry most, and the resistor only a small portion of the current. Crucibles to contain the molten metal might be employed, but these are distinctly limited in size. The simplicity and practicability of the electric arc for high-temperature melting have caused the arc furnace to find wide application in the steel industry.

A distinction should be made between electric sparks and electric arcs. Air is practically a nonconductor, but it is possible to create a high potential difference between two given points so as to cause a current to jump the gap and establish equilibrium conditions. These occur in electric storms and in various forms of electrostatic phenomena. In arcs the current also appears to pass through the air. It will be observed, however, that the necessary voltages are much smaller than those needed to cause sparks. The arc is formed between two carbon electrodes, but, in order to strike the arc, the electrodes are brought in contact, after which a gap may be gradually produced and the arc still maintained. If the gap should become too wide, the arc will break. Hence in arc furnaces some means of regulating the distance between the electrodes must be provided. In sparks the air or gas between the electrodes is a conductor, but it is not employed as such in arcs. Arc phenomena are explained on the assumption that some of the electrode material is vaporized by the heat of the arc, and that these vapors serve as the conductor. The arc gives us the highest temperatures yet obtained. The limit in commercial practice is set by the materials forming the electrodes and the materials of construction of the furnace body.

The intensity of the heat of the arc may be appreciated from the fact that carbon vaporizes at 3,500 to 3,600°C.

The temperatures reached in arcs between different electrodes are given in Table 76. Other than the atomic hydrogen form, the carbon arc is the hottest arc, making possible the concentration of a large amount of power in a small space. In a furnace, the temperature gradient between the arc and the furnace is high. The heat-transfer rate is a function of the differences of the fourth powers of the absolute temperatures of a radiant and a receptive surface. Part of the heat developed by an arc in the furnace is transferred by radiation directly to the charge and the remainder to the furnace walls and reradiated to the charge. Arc furnaces, therefore, have high melting rates.

Inasmuch as alternating current is commonly employed in arc furnaces, there being no electrolytic action desired, it is of interest to consider the arc itself. Fundamentally, if only a half cycle of alternating current be considered, the arc is a d.c. mechanism. In the direct arc the voltage and current are continuous. In the a.c. arc the current is started at the beginning of each half cycle by a hot cathode, and the instantaneous values of current vary during the half cycle. With each current reversal and at

TABLE 76. ARC TEMPERATURES[1]

Electrode	Arc Temperature, Degrees Kelvin
Carbon	3413
Tungsten	. 3000
Iron	2430
Nickel	2365

[1] COMPTON, *J. Am. Inst. Elec. Engrs.*, **46**, 1192 (1927).

the end of each half cycle the tips of the electrodes change their polarity, becoming alternately anode and cathode of the arc. Figure 195[2] shows the relationship between the effective arc voltages and effective current for an a.c. arc. The curve is similar to that of a d.c. arc in that increase of current is associated with decreased arc voltage. An arc operated from a constant-voltage circuit is inherently unstable.

The voltage needed to start a current through an arc gap is a function of the cathode temperature and the conducting ability of the atmosphere between the electrodes. The hotter the

[2] STANSEL, N. R., *Gen. Elec. Rev.*, **31**, 483 (1928).

cathode temperature and the better the gaseous medium as a conductor, the lower the starting arc voltage. If the atmosphere between the arcs be a material such as a metal vapor which is a good conductor, the current will start almost simul-
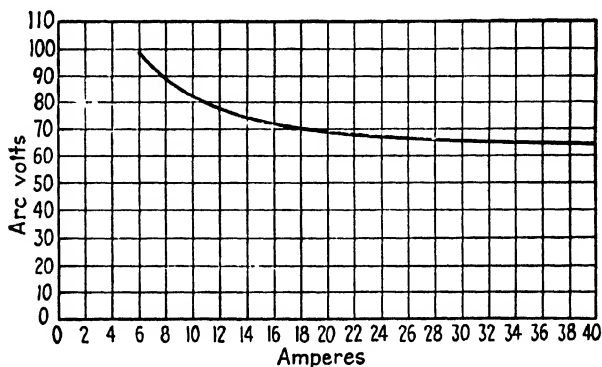
FIG. 195.   Volt-ampere characteristics of an a.c. arc.   (*Stansel.*)
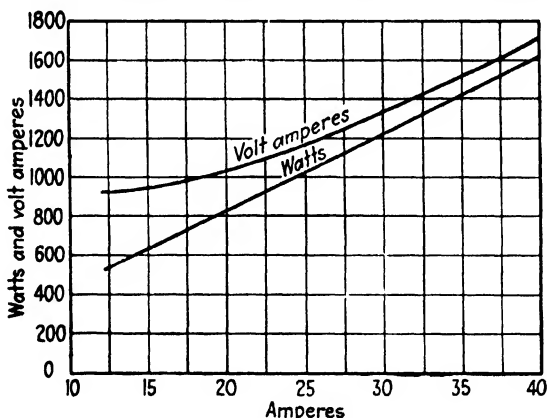
FIG. 196.   Change in arc power factor with change in watts in the arc.   (*Stansel.*)

taneously with the voltage. If the electrode gap be filled with slag or metal and slag, as in smothered arcs, lower voltages may result because of the higher conductivity of the intervening material.

Inasmuch as the tips of the electrodes during operation become dissimilar to a greater or less extent, there is usually a small amount of rectification of alternating current between carbon electrodes. This effect is so small that the operation of the arc is not influenced by the d.c. energy produced.

The power factor of a typical arc is given in Fig. 196 as the ratio of the watts to the volt-amperes. When all the influences are summed together, the power factor ·of the arc is generally above 85 per cent.

The a.c. arc when operating from a constant voltage circuit is rendered stable by a reactance in series. In the arc furnace, current variations, as long as the arc continues and power input is maintained, are not important, but voltage regulation of the power system depends upon the extent of current fluctuations
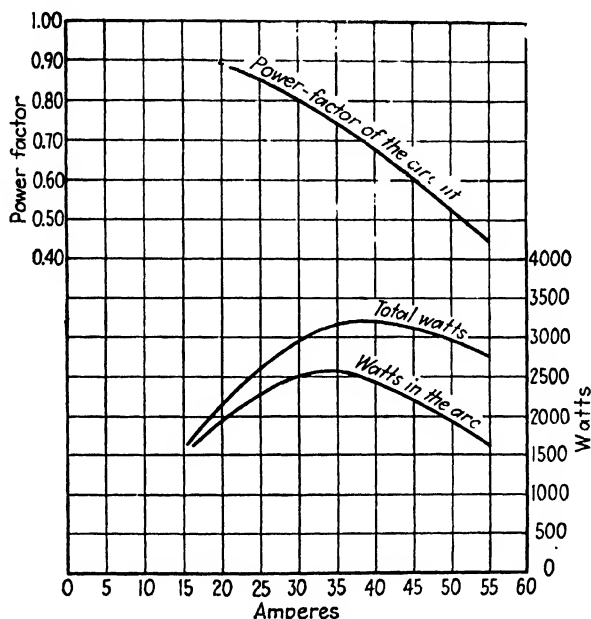
Fig. 197. Characteristics of the arc furnace circuit. (*Stansel.*)

in the system. The electrical characteristics of a small arc furnace are given in Fig. 197. Maximum power in the arc itself is given at a power factor between 75 and 80 per cent.

Modern electric furnaces are somewhat complicated mechanisms. To illustrate by example, the electric furnace most widely used in the steel industry is of the three-phase arc type. The complete electrical installation includes:

1. A transformer to step down the voltage of the power supply system to the voltage or voltages needed for the furnace. The transformer is ordinarily of the multitap type.

2. A secondary bus line and supporting structures between the transformer and the furnace.

3. Reactors, usually in the primary circuit of the transformer, to maintain arc stability and limit current fluctuations to the desired value if the reactance of the conductors be not sufficient to do this.

4. Switching apparatus for the control of the furnace, along with instrument and meter equipment.

5. Small d.c. motors with each electrode, with automatic regulators for the control of the electrode motors.

6. If direct current be not available for the electrode motors, a motor-generator set must be added to the list of apparatus.

7. Except in small hand-tilting furnaces, a tilting motor for the operation of the tilting mechanism.

It will thus be seen that the furnace proper, consisting of the shell, roof, electrodes, and tilting mechanism, is only a small part of the complete furnace setup.

In induction heating furnaces the bath or material to be heated is made to form the closed secondary circuit of an electric transformer. This secondary can then consist of but one coil. Electrical energy is supplied to a primary coil while the secondary circuit is formed by a ring of the metal under treatment, contained in an annular cavity which forms the crucible or container for the metal. When alternating current is applied to the primary coil, currents are induced in the closed secondary. Induction furnaces are divided into two classes, the coreless and the core type, the former being the general and the latter the specific case. The core type has a magnetic circuit of laminated sheet iron as in the transformer.

The current density in the secondary bears a fixed ratio to the number of turns in the primary coil. It is possible by variation of the impressed voltage to create heavy current density per unit of cross section in the secondary. Heating effects, in accordance with Joule's law, are then produced throughout the mass of the metallic bath. This method may also be considered an indirect resistance heating method in that the applied currents are induced but converted into heat by the resistance of the material under treatment. The metal under treatment may consist, instead of an annular ring, of charges in crucibles.

CHAPTER 21

ELECTRIC FURNACES FOR METAL MELTING

The early development of "electric" steel and the application of electric furnaces to steel metallurgy were stimulated chiefly by the desire to produce a product to compete with the expensive "crucible" steel. Because of the high fuel and labor cost of the crucible process, the small units and their short life, the electric furnace has achieved a large measure of success in this field, causing the abandonment of the crucible method. In the modern development of ferrous alloys, particularly of the stainless, nickel-chromium, vanadium, and tungsten types, of high-speed steels, and cutting tools, the electric furnace has found further application. It has definitely earned a place for itself in foundry work and steel-casting practice, as well as for some types of rail steels. The only part the electric current plays in the manufacture of steel is in the production of heat. For the development of this heat only two successful classes of furnace, the arc type and the induction type, are available. The advantages of electric-furnace application to steel metallurgy are the quick availability of the heat produced, the unusually high temperatures, the ease of regulation, the steady maintenance of any desired temperature, the cleanliness of the furnace and the method of heating, the nonproduction of harmful gases, the ease of control of the furnace atmosphere for the production of oxidizing, reducing, or neutral conditions, at the will of the operator. These electric-furnace characteristics permit the metallurgist to produce products of the highest quality from raw materials of any grade.

Furnace Arrangements and Types. Many different arc arrangements have been proposed by various inventors, as well as utilization of single-, two-, and three-phase circuits. Furnaces differ in the manner in which the current is introduced into the furnace and let out of it. This can be done entirely by electrodes entering through the roof or top, in which case there are as many arcs as electrodes and never less than two of each. In the

Heroult, 'Lectromelt, and Vom Baur designs as examples, the arcs are in series. In another type the bottom of the furnace may be built of such materials as to allow it to be used as an electrode, giving a direct-arc free-hearth-electrode furnace, an example of which is the Girod. In a modification of this design, the metallic (or conductor material) hearth electrode may be separated from the fluid charge by the refractory which forms the hearth lining. Although at room temperatures these refractories are insulators, at the operating temperatures of the steel-refining furnace they conduct. Considerable currents can then pass through the hearth. Such a construction results in the direct-arc buried-hearth-electrode type of furnace, as the Greaves-Etchells and Electrometals. In addition, other designs may combine electrode arrangements of two or more types, giving mixed types such as the Booth and the Nathusius. Instead of introducing electrodes through the roof of the furnace, they may be introduced through the side or through the sides and top, giving arcs between the electrodes, the heat being reflected down from the furnace roof to the bath or material under treatment. These are the indirect-arc type of furnace represented by the Stassano, the Rennerfelt, and the Detroit rocking furnace. The different classes of furnaces are illustrated diagrammatically in Fig. 198. The technically important designs, of which only the Heroult, 'Lectromelt, and the Detroit rocking type are important in the United States and Canada, will be discussed individually. Most of the other designs have been of European development and have found application there.

DIRECT SERIES ARC FURNACES

Three-phase Designs. The *Heroult* furnace has a bowl-shaped hearth similar to an open-hearth furnace with no electrical connections through the bottom. Electrodes pass through the roof and are suspended vertically so as to have the arcs in series. The current passes from one electrode to the bath and out through the other electrodes. Three electrodes are used for a three-phase furnace. The electrodes are carried on structures above the roof and are spaced in relation to each other so that arcs do not occur between them. The hearth slopes to a pouring lip. The entire furnace is enclosed in a shell of sheet steel, which
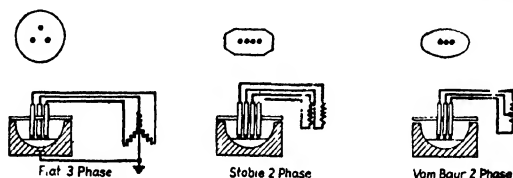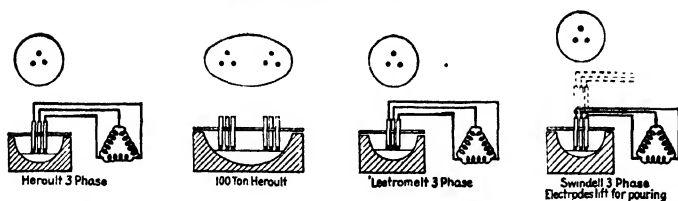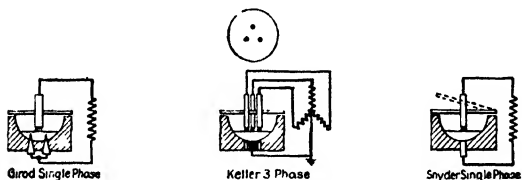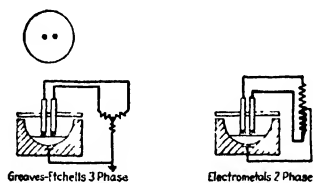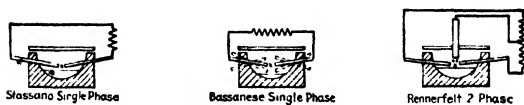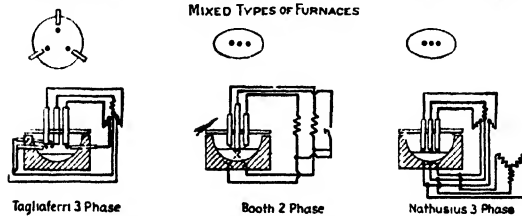
Fig. 198. Types of arc furnaces.

in turn is insulated from the furnace hearth and the refractory lining. Heating occurs through arcs between the electrode and the slag, the slag and the metal underneath, the current carried thus in series to the next electrode but passing through a layer of slag and forming a second arc as it passes between the slag and the electrode. Practically all the heat is formed by the arcs above the slag which acts as a shield to protect the metal from the carbon vapors thrown off at the bottom of the electrode and from the high temperatures at this point. Portions of this heat are transmitted to the metal through the slag and are distributed to all parts of the bath by conduction and convection. There is a slight motor effect produced by the current on the metallic bath. Single- and three-phase types are in use.

Heroult furnaces are designed in sizes from ½- to 100-ton capacities for open-top, chute, or machine charging. In the larger sizes six electrodes may be employed. Counterweight mechanisms for tilting were formerly used but have been replaced by rockers by which the center of gravity of the unit travels in a horizontal line when the furnace is tilting. These furnaces can be made either front or side tilt and, in addition to rocking forward, can be rocked backward. With the side-tilted furnace, charging can be done by a chute. Water-cooled copper tubing is used as busbars, eliminating trouble where electrode holders are connected, cutting down the skin effect, and thus increasing the efficiency of the conductors. The hearth on the Heroult is bowl-shaped, similar to an open-hearth furnace, with no electrical connections through the bottom, water cooled or otherwise. The circular shape gives maximum mechanical strength and minimum surface for heat radiation. Electrodes pass through the roof and are suspended vertically from a mast having as many arms as there are electrodes. The current passes from one electrode to the bath and out through the other electrodes. Three electrodes arranged at the points of a triangle are used for a three-phase circuit. The transformers have a number of taps on the secondary side so that a range of voltage is available.

Heroult electric furnaces are employed in making tool steel, special high-alloy steels, and high-speed steel; in the melting of high-priced nonferrous alloys and of ferromanganese for addition to open-hearth steel, and in the making of steel and iron castings. The charge consists of either cold scrap or partly refined steel

taken from bessemer converters or open-hearth furnaces, or of molten iron from cupolas.

Camp and Francis have given the details of Heroult furnace construction at the Duquesne plant of the U.S. Steel Corporation.[1]

It is estimated that 80 to 90 per cent of the electric steel produced in the United States is made in Heroult furnaces. It

FIG. 199.   A six-electrode 100-ton Heroult furnace.   (*American Bridge Company*.)

is now considered good practice to obtain a power consumption of approximately 500 kwhr per net ton in the making of acid steel castings in a 3-ton Heroult with an electrode consumption of 10 to 12 lb of carbon per net ton. In the making of alloy steels by the basic process in a 25-ton Heroult, the power consumption is approximately 525 kwhr per gross ton of good ingots. This has been bettered somewhat in the six-electrode 100-ton Heroult illustrated in Fig. 199. The 25-ton furnace shows an electrode consumption of $10\frac{1}{2}$ lb per gross ton of ingots. The electrodes are of graphite to carry the high currents employed in the furnace.

Modern developments in the manufacture of chromium steels,

[1] CAMP, J. M., and FRANCIS, C. B., "The Making, Shaping, and Treating of Steel," p. 386, Carnegie Steel Co., Pittsburgh, 1925, and later editions.

the nickel-chromium steels of the stainless and corrosion-resistant type, have increased the demand for electric furnaces. It is expected that the expansion of this industry will result in the development of still larger units.

The *Moore 'Lectromelt* furnace is similar in type to the Heroult, being of the direct-arc series type employing three electrodes operating on a three-phase circuit. While the Heroult has been used largely in steel refining, the 'Lectromelt has found its place in steel and iron foundry work. It is estimated that over 80 per cent of the electric-furnace foundry capacity is in 'Lectromelts. The furnaces are of the quick-melting type, generally using acid linings. Operating data show energy consumptions of 460 kwhr per ton of cold scrap charges, where no refining is done, to as high as 700 kwhr per ton, where some purification and refining of the material before casting is the custom. In foundry practice the electric furnace shows a 75 per cent thermal efficiency as compared to a 35 per cent value for a well-operated foundry cupola. The reducing atmosphere of the electric furnace makes possible the utilization of light scrap, turnings, borings, and similar low-cost materials not ordinarily suitable for open-hearth and cupola melting. A 3-ton 'Lectromelt is shown in Fig. 200.

A large number of furnaces have been brought forward employing the direct series arc principle. The furnaces differ in their electrical setup, manner of connection, hearth shapes, forms of shells, or electrode arrangements, as well as in other minor mechanical features. A few of these will be briefly discussed.

The *Swindell* furnace is a three-electrode three-phase direct series arc furnace with a balanced load on each phase. No bottom furnace connections are used. The electrodes do not tilt with the furnace when tapping, but are raised in a vertical position until they clear the furnace, after which the ports are covered and the furnace tilted. In this design the electrode masts are entirely separate from the furnace shell. Such an arrangement simplifies the construction and operation of the electrode equipment.

A multiple system of electrode melting furnaces has been developed for the continuous pouring of castings. Two furnaces are mounted on a revolving platform by which means the same transformer and set of electrodes are used for each

furnace alternately. Each furnace is complete in itself. No time is lost between melting periods, for as soon as the metal is ready to tap from the active furnace, the electrodes are raised, the table revolved, the other furnace placed in position under the electrodes, and the melting started coincident with the tapping of the first furnace. The electric melting can be made con-

Fig. 200   A 3-ton 'Lectromelt furnace.   (*Pittsburgh Electric Furnace Corporation.*)

tinuous, as the total time elapsing between "power off" on one furnace to "power on" on the second is less than 3 min.

The American *Greene* and the Canadian *Volta* may be classified as three-electrode three-phase direct series arc designs similar to the Heroult save for special mechanical and electrical features. They have found limited application. The Greene furnace shell is of reinforced steel construction mounted to roll over on the horizontal axis of the rolling cylinder shell in order to pour the metal.

The *Fiat* furnace is an Italian modification of the three-phase three-electrode direct series arc type. The hearth is hemispherical, mounted on two circular shoes of cast steel which allow rotation in any direction. Electrodes are graphite, arranged at

the points of a triangle. The hearth is slightly conductive. In practice it is connected with the center point of the star transformer connection on the secondary side and grounded. When phase loads are balanced, very little current flows to ground. Furnace voltages are 130 at the beginning of the heat to 75 at the end in the 5-ton unit. The application of the furnace has been limited to Italy and continental Europe, with no installations in the United States.

Furnaces with Electrodes in Line. The *Vom Baur* furnace had an elliptical hearth with three vertical electrodes in a straight line and was preferably operated with two-phase but could be employed with three-phase current.

The *Ludlum* furnace had a shell which was an elongated cylinder with conical ends for the pouring spout and charge doors, respectively. Three electrodes in a line along the axis of the cylinder entered through the segmental cylinder roof.

The *Stobie* furnace has found application in Great Britain but not in the United States. Data are tabulated as a direct-arc furnace in Table 78.

FREE-HEARTH-ELECTRODE FURNACES

In contradistinction to the direct-series arc type of furnace, other units have been developed in which the bottom of the furnace functions as an electrode. A number of arrangements have been employed, including the use of conducting materials as hearths; the insertion of conductors in the hearth, the conductors usually being of iron, so that they have free and exposed parts; and in other cases conductors buried in the hearth and covered by refractories which, at the operating temperature of the furnace, become sufficiently conductive to allow the passage of the current through them. Arcs are between the vertical electrodes and the hearth electrode, the current passing through the charge.

The *Girod* furnace was equipped with a plurality of electrodes, generally three, arranged vertically and automatically adjusted. Shells were cylindrical, having live bottoms consisting of a number of steel studs connected through the flat furnace bottom and refractories. The electrode system was arranged to be operated as three single-phase circuits with current flowing from

each electrode through the slag, through metal, and down through the studs at the bottom. In practice they were often operated with three electrodes with a three-phase connection. Moore[2] states that the furnaces were not designed for rapid operation, were slow, and were wasteful of power, electrodes, and refractories, so they are no longer used in the United States.

The *Keller* furnace used in Europe had a composite hearth of iron grids with magnesite and tar rammed between bars.

The *Snyder* furnace was based on the work of Siemens in England in 1878 on a single-phase, single vertically adjustable electrode furnace with a bottom water-cooled electrode. Graphite electrodes of small size with arc voltages of 110 to 220 resulted in small currents and rather long arcs. The shells were relatively high to overcome the destructive effect of a long arc, the doors kept at a low level and as nearly gastight as possible for protection of the roof. To save time during operation, the furnace carried a simple mechanism pivoted for pulling back the roof, so that, by means of the same mechanism that tilted the furnace forward for tapping, the roof might be tilted backward to permit rapid charging.

BURIED-HEARTH-ELECTRODE FURNACES

During the First World War the *Greaves-Etchells* furnace, built with a rectangular rocking shell, was introduced. This furnace was fitted with one or more unbalanced three-phase circuits consisting of two upright vertically adjusted electrodes and a bottom contact extending from the shell into the bath. The voltage on the bottom electrode was of a lower order so as to balance the current between the bottom and the two top carbon electrodes. This system of electrodes was multiplied on the larger furnaces, consisting of two, four, or six top electrodes, each with a corresponding bottom contact, each set of electrodes having its own transformer group so that on the larger furnaces the unbalance which was unfavorable in the small furnaces could be more or less compensated.

These furnaces were invariably built in rectangular shells, and their roofs were made of standard-shape refractory rectangular blocks, so that very heavy construction was essential to

[2] MOORE, W. E., *Trans. Electrochem. Soc.*, **60**, 173 (1931).

minimize warping and expansion.   Moore states that they were comparatively slow in operation, high in power and electrode consumption, and unbalanced in load.

The *Electrometals*, also known as the Grönwall-Dixon furnace, had a cylindrical flat bottom shell similar to the Heroult design and mounted on rockers.   Four vertically adjustable electrodes entered through the roof, were connected to a four-phase star electric circuit with a neutral grounded in the furnace bottom. The transformer system was a Scott two-phase three-phase connection.

INDIRECT-ARC FURNACES

The discussion up to this point has been confined to the direct-arc types of electric furnaces applied to iron and steel.   In the indirect-arc type, the arcs are between electrodes and not between electrodes and slag, or electrodes and charge, or electrodes and hearth through the charge.   The *Stassano* furnace had three downwardly inclined electrodes entering from the sides of the cylindrical shell and made a so-called "free-burning" or "blowing" arc, intended to blow down (by magnetic reactions) onto the bath and hearth.   Moore[3] states that the radiation in an upward direction was so intense from these inclined electrodes that it was difficult to keep refractories in the roof or upper parts of the furnace shell unless the furnace was operated at a slow rate.

The *Bassanese* furnace is a modification of the Stassano, having its electrodes mounted on mechanisms which make possible the use of direct as well as indirect action of the arc on the bath.   The electrodes are inclined to a variable angle so that the arc may be made free burning or directly projected on the metal.   One-ton furnaces are single phase; 3-ton units are two phase connected by Scott transformers to three-phase supply. Furnace voltages are 160 to 170, being higher than in the Stassano type.   The units tilt for pouring.

In the *Angelini* modification of the Stassano, the electrodes are arranged so that arcs may be formed between movable electrodes above the metal surface, as well as between each electrode and the metal.   This arrangement permits the use of single-phase currents at higher voltages than those employed in other designs.   Electrode regulation is by hand.

[3] *Ibid.*

The *Rennerfelt* poly-phase electric furnace has a boxlike rectangular shell with three electrodes of the indirect-arc free-burning type.   One electrode extends in through the top, and two others are mounted horizontally through the sides of the furnace.   Power is from a two-phase three-phase Scott connected transformer with the common return being the vertical
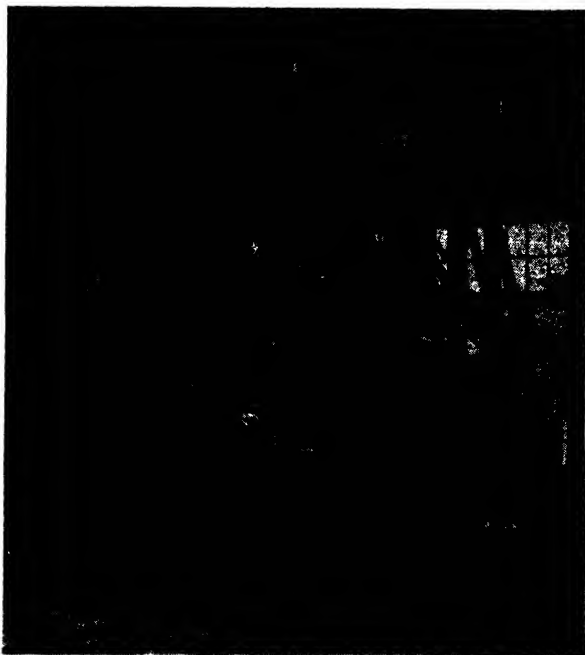
Fig. 201.   A 1,200-kva Rennerfelt furnace.   (*Ivar Rennerfelt.*)

electrode through the roof.   Figure 201 illustrates a Rennerfelt furnace, and operating data are given in Table 78.

MIXED TYPES OF FURNACES

The *Tagliaferri* furnace combines the indirect with the direct series arc for two- or three-phase circuits.   The three-phase unit has three roof and three auxiliary side electrodes.   In refining, it is a direct series arc unit.   In melting, arcs are sprung between roof and side electrodes.

In the *Booth* furnace there are one, two, or three roof electrodes for one-, two-, or three-phase circuits, as well as hearth electrodes.   There is an individual hearth electrode for each

roof electrode, but it is located on the opposite side of the furnace instead of being directly underneath the bottom of the roof electrode. An auxiliary roof electrode is provided, connected with the return to the transformer in parallel with the hearth electrode. In furnaces of 100- to 3,000-lb capacity, transformers are of the Scott connected type, three phase to two phase.

The *Nathusius* furnace combines the principles of the direct series arc, the buried-hearth type, and the resistance idea. The furnace charge is heated from above by arcs and from below by currents through the hearth electrodes. The latter type of heating can be independently regulated through star transformer connections to the hearth electrodes, independent of those through the roof. The hearth as well as the whole of the charge may be included in the circuit as an ohmic instead of an inductive resistance. Three-phase currents are used, the transformer secondaries being star-connected to the roof electrodes, and their separate returns to the corresponding ones in the hearth. The metal bath in the furnace thus becomes the neutral point of the transformer.

INDUCTION FURNACES FOR IRON AND STEEL

The first induction furnaces were made around 1890. An induction furnace of the open-ring type was built by Kjellin in Sweden in 1891.[4] It consists of a transformer assembly with primary coil, iron core, and secondary circuit of ring type of uniform cross section over its entire length. The molten metal, which forms the secondary circuit, is contained in a horizontal trough of refractory material. In this type of furnace, the level of the metal contained in the trough varies within a wide range from the beginning to the end of the melt. The trough cannot be emptied completely. A heel of molten metal is maintained therein at all times, and when melting is started, ingots are charged into the trough, thereby increasing the level of the molten heel. The resistance and the reactance of the secondary are thereby reduced, and the furnace will take less power at the beginning and more power at the end of the melt.

These conditions are by no means ideal because the power

---

[4] RODENHAUSER, W., SCHOENAWA, J., and vom BAUR, C. H., "Electric Furnaces in the Iron and Steel Industry," 3d ed., John Wiley & Sons, Inc., New York, 1920.

absorbed by the furnace during the operation fluctuates too much, thereby seriously affecting the over-all load factor of the furnace. An ideal furnace should draw steady power.

A disadvantage of the ring-type induction furnace is the low power factor. The power factor of this furnace was so poor that very low frequencies had to be used for correcting the power factor. Frequencies down to 5 cycles per sec were suggested for furnaces of large capacities, and therefore large motor-generator sets were used. These furnaces were used at that time chiefly for melting steel.

The *Kjellin* furnace is shown diagrammatically in Fig. 202. The laminated soft-iron core formed a closed circuit. The primary section was built of either air-cooled copper wire or water-cooled copper tubing. A ring-shaped refractory-lined channel was the secondary. The entire furnace was enclosed in a steel shell. Molten material must always be left in the furnace for successive operations. Commer-

Fig. 202. Kjellin furnace.

cial units up to $8\frac{1}{2}$ tons, operating on frequencies of the order of 5 cycles, have been built.
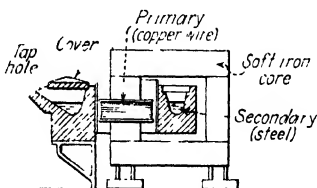
Operating data for a 2-ton furnace showed a consumption of about 170 kw at 3,000 volts in the primary and 30,000 amp in the secondary. Power consumptions were of the order of 750 to 850 kwhr per ton of steel with cold charges of pig iron or pig iron and scrap.

The *Röchling-Rodenhauser* furnace design eliminated some of the disadvantages of the Kjellin furnace—*i.e.*, small capacity and low power factor—by the application of a combination induction and resistance principle. A diagrammatic representation of the furnace is shown in Fig. 203. The unit consisted of an iron core with two primary windings and a secondary in the form of a lemniscate broadened in the middle to form a hearth. Auxiliary secondary windings heated the central hearth. An air gap separated the primaries and secondaries. Hearth electrodes at opposite sides of the central hearth were connected to the auxiliary secondary sections.

Single-phase furnaces rated at $8\frac{1}{2}$ tons took 700 to 750 kw at

4,000 to 5,000 volts. Three-ton furnaces showed power factors of 0.7 to 0.8 at a frequency of 25 cycles. With molten charges, about 120 to 160 kwhr per ton was consumed for refining of bessemer steel, while for reduction of the sulfur and phosphorus to 0.01 per cent, 200 to 300 kwhr was required. On cold scrap the power consumption was of the order of 900 kwhr per ton.

In the United States the use of the induction furnace for ferrous metallurgy has been limited; but in the form of the Ajax-Wyatt, Ajax-Tama, and Ajax-Northrup induction furnaces
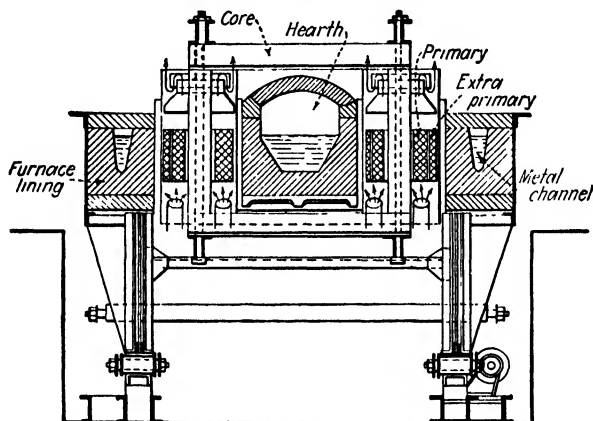
Fig. 203. Vertical section of the Röchling-Rodenhauser furnace.

it has been employed in nonferrous metal melting. The high-frequency furnace has found greater application in steel and ferrous alloy manufacture, particularly on a small scale and for special materials.

An induction furnace may be described as a step-down transformer in which the metal under treatment is the short-circuited secondary coil or coils. The induction furnace is subject to the magnetic and electrical losses due to hysteresis in the iron core in the same manner as transformers. The design of the furnaces is such that magnetic losses are usually greater than those in transformers, with resulting lower power factor. It is impossible to bring the primary and secondary in a furnace so close together that all lines of magnetic flux are cut by both of them. This is due to insulation and the necessity of cooling the core and the primary. In addition, there is considerable self-induction in the primary because of magnetic leakage of lines which are cut only

by the primary and not by the secondary. The steel is in a ring-shaped channel, through the center of which the primary coil and the core pass, and is the one turn secondary of the circuit. The steel is thus a short-circuited secondary of low resistance in which high-amperage currents are induced and the steel heated by the I^2R effect.

A large number of arrangements of primary and secondary have been proposed. Some have been used for a short time while others were never put into technical application.

COMPARISON OF FURNACE TYPES

The direct series arc, the indirect arc, the free- and buried-hearth electrode, the mixed types, and the low-frequency induction electric furnaces designed for iron and steel melting and refining are compared in Table 77. The advantages and disadvantages of each type are emphasized.

Modern electric furnaces are ordinarily supplied with transformers so designed that better operating conditions may be obtained from the viewpoint of the user and the power company. Transformers for arc furnaces differ mainly from power transformers by having a considerable number of taps to obtain a range of secondary voltage. This permits the use of higher voltages during the melting of the steel charge than those needed for the refining period. These transformers are of sufficient capacity to permit rapid melting and are able to withstand heavy loads without overheating. They are provided with large reactances to choke back current surges.

Successful furnace operations depend more or less upon speed of production, which in turn is affected by speed of charging, handling, refining operations, and making repairs and adjustments during pouring as well as during melting. Greater speed results in larger production, more efficient operation, lower refractory and electrode costs, lower power consumption, and reduced metal losses.

Rapidity of operation is a function of transformer capacity, but not entirely so. The range of available secondary voltages has a marked effect. Speed of electrode control and transfer is important, in that the quicker the arc is again formed after being broken, the less will be the loss of time and energy.

Hearth design to give uniform heat application, so that hand

TABLE 77. COMPARISON OF ELECTRIC-FURNACE TYPES

Series arc 1	Indirect arc 2	Free-hearth electrode 3	Buried-hearth electrode 4	Mixed types 5	Induction (low frequency) 6
ADVANTAGES					
Simplicity		Simplicity, but less than 1 and 2	Simplicity, but less than 1, 2, 3	Flexibility of operation	No electrodes
Higher slag temperatures than induction type; ability to employ high melting point slags and maintain them in fluid condition					No external transformers and cables
Reducing atmosphere due to electrodes; high power factor					
Higher voltages and smaller currents used than in 2, 3, 4	Can be operated quietly without large load fluctuations	Can be started more quickly and quietly than series arc		Operation and regulation to suit particular conditions	Lower metal vaporization loss than arc types is claimed
No water cooling of hearth			No water cooling of hearth	No water cooling of hearth in certain forms	
Can be built in very large sizes; adaptable to refining large charges of impure materials		Current through bath aids heating (?)	Heating effect of hearth aids in rapid refining. Hearth resistance exerts buffer effect on load fluctuations	Rapid melting due to special arrangements	Less severe action on roof
			Better metal circulation claimed (?)		
DISADVANTAGES					
Electrodes, and their regulation; complicated controls (has been overestimated)					
Electrode oxidation and maintenance					
Labor requirements higher than other arc types		Water cooling of hearth electrodes	Electrical arrangement and furnace operation not as simple as 1		Low power factor
					Small size
Heat losses through electrodes higher than series arc		Lower voltages and higher currents than 1			Low frequencies are used (special electrical equipment necessary)
Possible maximum size limited					Heavy wear on metal channels
					Lower slag temperatures; longer time needed for refining
Slower in refining than 1, 3, 4, 5					Bulky furnaces

raking of the charge is avoided, increases melting speed. The same holds true for mechanical devices such as closely fitting doors, closed roofs, and other constructional features which reduce heat losses. In this connection too much importance cannot be placed upon mechanical devices for speedy charging. The more rapidly a furnace is charged, the less will be the cooling effect of cold air entering the furnace, causing refractories to spall and deteriorate. Cold air coming in contact with the white-hot electrodes oxidizes them rapidly. Mechanical features for rapid pouring and emptying of the furnace affect power consumption and speed of operation.

With the exception of small-size units, modern electric furnaces have electrical devices which regulate the power supply, automatic controls on the electrodes, as well as load equalizing devices for the different electrodes.

Operating data of various types and makes of electric arc furnaces have been gathered together in Table 78. These figures have not been brought together for strict comparison purposes, in that, for example, the power-consumption figures are not easily comparable owing to differences in size of the furnaces, type of charge, quality of the resulting product, the power supply, as well as special operating conditions pertaining to certain types and not to others. In the United States the three-electrode three-phase series-arc furnace is used more largely than any other.

ELECTRIC FURNACES FOR NONFERROUS MELTING

Electric furnaces for nonferrous melting developed along three general lines conforming to three basic electrical principles. The three types now in use may be roughly divided into arc, resistance, and induction furnaces. The third class is generally subdivided into furnaces of low-frequency type and those in which high-frequency currents are employed. Commercial use of electric brass and bronze furnaces dates from about 1916. Development work prior to that time was along experimental lines and served to demonstrate the possibilities of electric melting. Dozens of different types of furnaces were designed and built, both before and after electric melting became established. Only a few of them proved worthy of further development. Those now recognized as possessing commercial value have dwindled to but a few types, namely, the indirect-arc rocking furnace, such

TABLE 78. OPERATING DATA OF ELECTRIC FURNACES FOR IRON AND STEEL

Characteristics	Bassanese	Booth	Brown Boveri Heroult	Electrometals	Fiat	Girod	Greaves-Etchells
Type of furnace	Indirect arc	Mixed	Direct series arc	Buried hearth electrode	Direct series arc	Free hearth electrode	Buried hearth electrode
Minimum size, tons capacity	....	1/9	7/10	1½	1	....	½
Maximum size, tons capacity	....	1½	25	30	15-18	15	60
Number of phases	2	3	3	2	3	1[1]	3
Number of electrodes	....	3	3	2	3	1[1]	2 or 4
Electrode regulation	....	Manual	Hydraulic	Mechanical	Automatic	....	Manual up to 1 ton; Automatic for 1½ ton up
Transformer connection	Scott	Scott	Delta-star	Scott	Star	1 phase	Delta-star
Kilowatt-hours per ton, cold charge	700-1,000	500-700	600-800	550-600	680-800	700-800	600-900
Kilowatt-hours per ton, hot charge	....	....	....	....	....	250-350	70-150
Electrode consumption, lb. per ton, cold charge	25-30	....	7.5-12	12-16[1]	4-5	17-30	7-10 (graphite) 12-15 (castings)
Electrode consumption, lb. per ton, hot charge	....	....	....	....	....	10-15	1-2 (graphite)
Form of shell	Circular	Oval	Circular	Rectangular	Circular	Oval	Rectangular up to 5 tons Circular for 7½ tons up
Electrode arrangement	Through sides	In line	Triangle	....	Triangle	Centrally	In line up to 5 tons Square for 7½ tons up
Shape of hearth	Circular	Oval	Circular	Elliptical	Circular	Rectangular[1]	Oval or round
Life of roof, number of heats	.	....	100-150	....	110	....	120-180
Melting loss, cold charge	.	....	4-8%	....	5-8%	5-6%	5-8%
Melting loss, hot charge	.	....	....	....	....	....	1%
Charging doors	.	1 at end	1 or 2	1 or 2	1 at back	....	1 or 2
Pouring arrangement	Tilts forward	Tilts endwise	Tilts forward	....	Tilts forward	Rolls forward	Tilts forward

TABLE 78. OPERATING DATA OF ELECTRIC FURNACES FOR IRON AND STEEL.—(*Continued*)

Characteristics	Greene	Heroult	Keller	Lectromelt	Ludlum	Rennerfelt
Type of furnace	Direct series arc	Direct arc, series arc	Free hearth electrode	Direct series arc	Direct series arc	Indirect arc
Minimum size, tons capacity	¼0	½	......	½0	5	1
Maximum size, tons capacity	50	120	......	50	10	8
Number of phases		3	1	3	3	2
Number of electrodes	3, 6	3, 6	1	3	3	3 or 6
Electrode regulation	Automatic	Mechanical, automatic	......	Mechanical, automatic	Automatic	Hydraulic
Transformer connection	......	3 phase delta-delta or delta-star	1 phase, 2 taps	3-phase delta	Star-star	2–3 phase Scott
Kilowatt-hours per ton, cold charge	500–800	460–700 (castings) 600–1,000 (tool steel)	275–350	460–700 (castings) 600–1,000 (tool steel)	600	670–1,000
Kilowatt-hours per ton, hot charge	100–300	100–400	......	100–400	......	......
Electrode consumption, lb. per ton, cold charge	10–15	10–13 (castings) 20–40 (special steels)	23–30	10–13 (castings) 20–40 (special steels)	15	9–13
Electrode consumption, lb. per ton, hot charge	......	10–15	......	10–15	......	......
Form of shell	Circular Triangle	Circular² Triangle	Rectangular	Circular Triangle	Elliptical In line	4–6 Rectangular 2 or 4 through sides, 1 or 2 through top
Electrode arrangement						Elliptical
Shape of hearth	Round or rectangular 300–2,000 acid 150–300 basic	Circular²	Rectangular	Saucer	Elliptical	200
Life of roof, number of heats	......	......	......	600–700	60	4%
Melting loss, cold charge	......	......	......	......	4.5%	1 or 2
Melting loss, hot charge	......	......	......	......	......	
Charging doors	1 opposite spout	2 at sides	......	2, opposite	2 at ends	
Pouring arrangement	Hydraulic tilting	Tilts forward to lip	......	Tilts to either door	Tilts endwise	Tilts on rockers

TABLE 78. OPERATING DATA OF ELECTRIC FURNACES FOR IRON AND STEEL.—(Continued)

Characteristics	Snyder	Stassano	Stobie	Swindell	Tagliaferri	Volta
Type of furnace	Free hearth electrode	Indirect arc	Direct series arc	Direct series arc	Mixed	Direct series arc
Minimum size, tons capacity	1	....	½	¾	....	¼
Maximum size, tons capacity	5	15	30	25	30	25
Number of phases	1 or 3	1 or 3	2 or 3	3	3	3
Number of electrodes	1 or 2	2 or 3	3, 4, or 6	3	6	3
Electrode regulation	....	Manual	Automatic	Automatic	....	Automatic
Transformer connection	2–3 phase	3-phase delta	Scott or delta-star	Delta-delta	3 single phase	Star-delta
Kilowatt-hours per ton, cold charge	600–1,000	700–1,000	600 average	500 up	580–850	500–550
Kilowatt-hours per ton, hot charge	350	....	140 average	70 up	100–300	150–200
Electrode consumption, lb. per ton, cold charge	10–15	20–30	6.1–7	4½ up	....	Carbon 10–11 Graphite 7–8
Electrode consumption, lb. per ton, hot charge	....	....	2 average	1	....	Carbon 4–5 Graphite 3–4
Form of shell	Oval	Circular	Octagonal or circular	Circular	Circular	Circular
Electrode arrangement	Centrally	Through sides	In line	Triangle	Through top and sides	Triangle
Shape of hearth	Oval	Circular	Circular	Circular	Circular	Circular
Life of roof, number of heats	200	120–150	150	1,100 downward	....	200–300
Melting loss, cold charge	....	2%	2.5–3%	3% up	....	2.5–3%
Melting loss, hot charge	....	....	1%	1.5% up	....	None
Charging doors	Hinged roof	....	1–3	1	....	2 at side
Pouring arrangement	Rolls forward	Tilts forward	Tilts to pour	Motor driven tilting mechanism	....	Tilts forward

[1] Large sizes three phase, three electrodes, circular hearth.
[2] Graphite.
[3] Large furnaces oval.

as the Detroit; the vertical-ring low-frequency induction furnace, such as the Ajax-Wyatt; and the high-frequency induction furnace, such as the Ajax-Northrup. An indirect-arc rotating furnace, an example of which is the Booth, and a granular carbon resistance unit of which the Baily was typical were manufactured in relatively large numbers for a time. Their production was gradually discontinued in favor of more rapid, efficient melting units of better design. In addition, some of the furnaces discussed under iron and steel, particularly the indirect-arc Rennerfelt, have found considerable application in Europe in connection with nonferrous melting

In comparison with other methods of melting, electric furnaces can be designed to allow control of furnace atmosphere, as well as to offer the possibility of obtaining exact temperature control under uniform temperature conditions. As a result, oxidation and volatilization losses are reduced, more rapid heating and working are possible, with resultant better melting conditions and in many cases lower costs.

The temperatures required in nonferrous melting are as a rule lower than in steel practice. When zinc is an alloy constituent, direct-arc furnaces are seldom employed. In general a successful steel-melting furnace is not applicable to nonferrous melting. In many cases the reverse is true, that furnaces originally designed for nonferrous melting are finding successful application in melting cast iron, as in the case of the Detroit, and in steel, particularly of the tool and special alloy type as in the case of the Ajax-Northrup.

In electric furnaces for metal melting, the physical and electrical characteristics of the metals themselves are important. Figure 204 shows the values of the specific resistivities of different metals in the molten state. The metals of very low resistivity are silver, copper, aluminum, and gold. The metals of higher resistivity are mercury, lead, and nickel. All the other metals have resistivities lying between these two extreme cases. All the metals show a sudden increase of resistivity at the melting point. Manganese behaves differently. It shows a decrease of resistivity at different phase changes, including the transition from the solid to the molten state, according to Grube and Speidel.[5] The resistivity of alloys in the molten state cannot be deter-

[5] GRUBE, G., and SPEIDEL, H., *Z. Elektrochem.*, **46**, 233–242 (1940).

mined from the resistivity of the component parts. Special measurements have to be made from case to case.

The energy required for melting metals, usually called the "heat content," consists of three parts: (1) the heat required to raise the temperature of the solid metal to the melting point; (2) the latent heat necessary to change from the solid to the
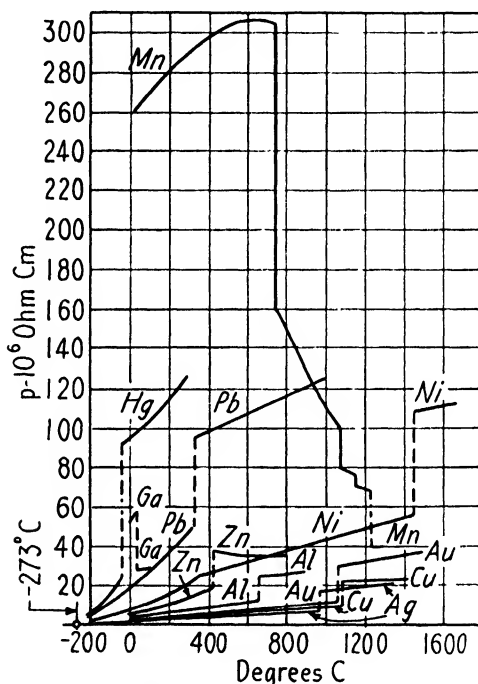
FIG. 204.   Specific resistivity of pure metals in solid and molten states.

molten state at the melting temperature; (3) the heat needed to raise the molten metal to the desired pouring temperature. The total amount of heat thus required is usually plotted in charts, like that shown in Fig. 205, which gives in solid lines the heat content of the principal metals (aluminum, copper, iron, and zinc) in terms of kilowatthours per pound at different temperatures. It will be noted that aluminum needs much energy per unit of weight for melting and is surpassed only by iron.

However, inasmuch as many of the physical characteristics of metals, such as tensile strength and electrical conductivity, are

not judged by weight, it is also interesting to plot the heat content in terms of kilowatthours per cubic foot, *i.e.*, in terms of energy per unit of volume.   Figure 205 also shows the heat content of the same metals plotted in this manner in dotted lines, and it will be seen that aluminum has a low heat content per unit of volume as compared with the other metals.

Arc Furnaces.   In the *Detroit* electric furnace, also known as the "rocking" furnace, heat is produced by an arc drawn between two electrodes extending through opposite end of a horizontal.
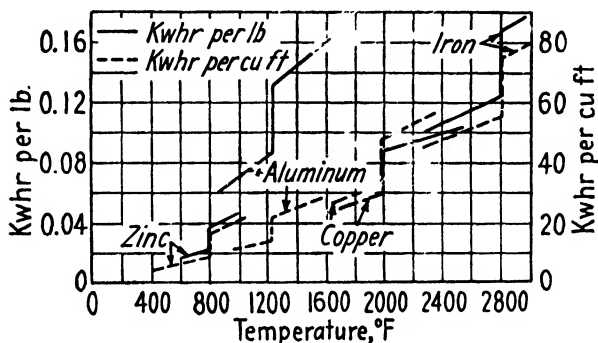
FIG. 205.   Heat content of zinc, aluminum, copper, and iron expressed in terms of energy per pound and per cubic foot.

cylindrical, refractory-lined steel chamber which is supported on rollers and automatically rocked backward and forward by an auxiliary motor mounted on the furnace base.   The furnace is tapped through a spout and charged through a door which is removable, the spout and door being combined in one opening in the side of the shell.   Power is supplied from a transformer connected through flexible leads to electrode clamps supported from either end of the steel shell.   The electrodes are of graphite, varying in size with the load on the furnace.   Power input to the furnace may be varied by hand regulation of the arc between the electrodes.   During charging, the electrodes are withdrawn until their ends are flush with the refractory wall.   In operation, rocking of the furnace is started when melting of the charge has begun.   Furnaces are built in sizes from 250- to 3,500-lb charging capacities, with connected loads of 75 to 400 kva, single-phase 60-cycle current being employed.   The smaller units are capable of turning out heats in 15 to 25 min, the larger ones from 45 to 60

min. Because of their steadier operation the smaller furnaces have slightly higher melting efficiencies than the larger ones. Power factors of 75 to 85 per cent are usually maintained. The power consumption differs somewhat with different alloys. In a typical case of an 85 per cent Cu, 5 per cent Sn, 5 per cent Pb, and 5 per cent Zn, good operating data show 285 kwhr per ton, an electrode consumption of 3.25 lb per ton, lining life of 1,000
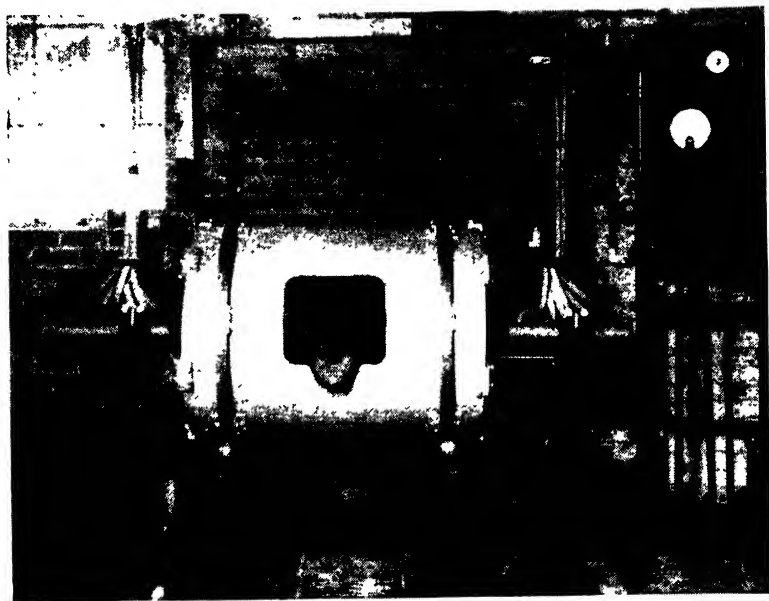
Fig. 206. A 300- to 350-lb Detroit electric furnace. (*Detroit Electric Furnace Company.*)

heats, and a metal loss of 0.5 per cent. Figure 206 shows the construction of a typical small furnace. Typical operating data are given in Table 79.

The rotating or *Booth* furnace resembled the rocking type in general appearance with the exception that the horizontal cylindrical shell revolved continuously in one direction instead of being rocked. As a result, collector rings were needed to bring power to the electrodes entering through the ends of the cylindrical shell. The metal charge could not be stirred until it was entirely melted; otherwise pieces of metal would drop against the electrodes and break them. A tap hole was provided at one end of the shell and a door surrounding the electrodes at the

opposite end was used for charging. To avoid leakage of metal, the tap hole had to be kept tightly closed during the rotating period. Furnaces were single phase similar in capacity to the Detroits but showing somewhat higher energy and electrode consumptions and metal losses. The inconveniences encountered in charging and discharging retarded its commercial application.

Induction Furnaces, Low Frequency. The core-type induction furnace operates on the principle of a short-circuited transformer. Figure 207 shows the fundamental parts of the electric
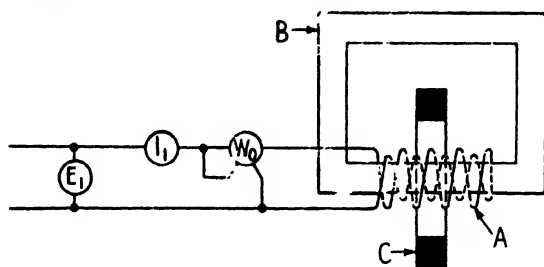
FIG. 207. Fundamentals of electric circuit. *A*, primary coil; *B*, magnetic core; *C*, secondary coil holding the metal.

circuit. Alternating current of power-line frequency is applied to the primary coil *A*, made of high conductivity material. The coil surrounds a laminated core *B*, made of low-loss high-saturation steel. The ring *C*, surrounding the primary coil, represents the molten metal which is contained in a receptacle of refractory nonconductive material.

If an alternating emf E_1 be applied to the primary coil having n turns, a primary current I_1 will flow through. At the same time a secondary current of the magnitude $I_1 \cdot n$ will flow through the molten metal loop *C* in the opposite direction. The secondary current is usually very large and creates heat in the secondary circuit, having a resistance R_2, according to Joule's law

$$W_0 = I_1{}^2 \cdot n^2 \cdot R_2$$

If the heat thus generated is larger than the heat losses of the apparatus, the temperature will rise until equilibrium is attained. There will always be an equilibrium temperature for each particular apparatus. The energy required to hold the molten bath at a constant working temperature (usually called the "idling power" W_i) can easily be measured in furnaces provided with

automatic temperature controllers. It is only necessary to set a certain temperature on the controller and to measure the energy with the wattmeter or the watthour meter. The efficiency of the furnace is given by the equation

$$ l = \frac{W_0 - W_i}{W_0} $$

where W_0 is the operating power and W_i the idling power. W_i consists of copper and iron losses in the transformer which are very small and, further, of heat losses through the furnace walls and through the opening of the furnace. The heat losses through the metal walls are determined by the dimensions of the walls and the heat conductivity of the refractory and insulating materials used for their construction. A temperature drop must be allowed within the refractory walls, and therefore a certain amount of heat losses must be taken into account.

A large temperature gradient within the refractory prolongs to a large extent the life of the lining, and this again depends upon the nature of the metal to be melted. Metals attack refractories differently, some vigorously, others to a lesser degree. In dealing with metals which are very destructive to the lining, it is often necessary to allow for a larger temperature drop or heat flow through the refractory walls to ensure a longer life of the refractory. The heat losses through the charging openings of the furnace increase with the fourth power of the absolute temperature of the metal and depend, further, upon the size of the opening and the emissivity coefficient of the metal bath.

The *Ajax-Wyatt* enclosed vertical-ring type has found application for brass melting. It operates on the transformer principle in which a molten ring or loop of metal contained in a refractory channel acts as the secondary of the transformer, while the primary is an adjacent coil connected to a power line. The furnace is shown diagrammatically in Fig. 208. The primary coil extends through the base of the lower portion of the furnace chamber and surrounds a furnace core. The primary coil and core are surrounded by a refractory block through which runs a V-shaped ring or channel. At the top the so-called "ring" opens into the furnace chamber. The molten metal in the main chamber therefore exerts a static pressure on the metal in the channel, overcoming the "pinch" effect which in the horizontal channel

furnace tends to interrupt the current flow. The pinch effect is the tendency of a conductor to contract due to magnetic influence when a current is passed through it. Its force is proportional to the square of the current and is more evident in low-resistance conductors. When currents are passed through molten metal, the pinch effect may be sufficiently strong to separate the molten conductor and break the circuit. The only ways of overcoming the pinch effect involve either the reduction of the current or the application of a counteracting pressure on the molten metal.

Stirring action is caused in the Ajax-Wyatt furnace by the motor effect, a magnetic

Fig. 208. Ajax-Wyatt induction furnace.

pumping or repulsion action which tends to circulate the metal. The V-shaped channel increases this action.

The Ajax-Wyatt furnace has found application in rolling-mill practice where copper-zinc alloys are made. It is estimated that considerably more than 90 per cent of brass in rolling mills is electrically melted, and about three-quarters of this is done in Ajax-Wyatt furnaces, the rest in Detroits. In addition, the furnace has been applied to rolling-mill practice for other alloys such as those of the nickel-copper type, and the melting of pure metals such as zinc. In foundry practice the Detroit furnace is estimated to account for over 80 per cent of all the nonferrous alloys electrically melted, because it can start with cold charges. The Ajax-Wyatt cannot be completely tapped, and it is necessary to charge the furnace with molten metal when it is first started. When production is interrupted, the furnace must be completely discharged or else sufficient energy must be fed to it so as to keep the metal in the channel molten. The standard size Ajax-Wyatt is 60 kw, 440 or 220 volts single phase, designed to hold 1,000 to 1,150 lb of molten metal of which 600 to 750 are tapped at each heat. The balance is left in the furnace to fill the channel and

close the circuit across the loop. Transformer capacity is 60 to 125 kw, with variable secondary voltages. Operating data on the furnace under various conditions are given in Table 79.

It was a long time before the submerged-resistor type of furnace could be adapted for the commercial melting of aluminum and aluminum alloys. The difficulty lay chiefly in the low specific gravity of aluminum alloys. In the heavy metals, the slags or nonmetallic particles contained in the melt are much lighter
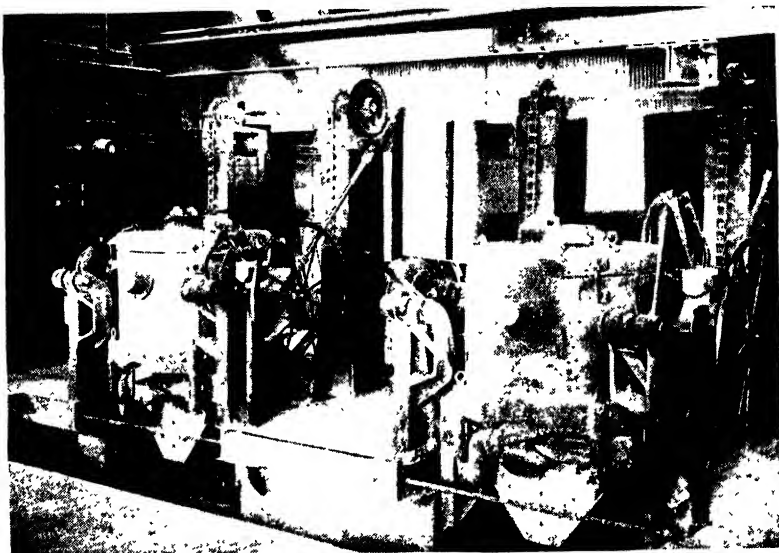
FIG. 209. Two 80-kw 1,000-lb Ajax-Wyatt furnaces. (*The Ajax Metal Company.*)

than the metal, so that they tend to float on the surface of the bath. In the light metals the slag particles have about the same specific gravity or are heavier than the melt. If nonmetallic nonconductive particles are contained in the secondary loop of an induction furnace, they tend to increase the resistance of the secondary and to change the characteristics of the furnace.

Such slag particles tend to stick to the walls of the melting channels and gradually to decrease their cross section. When attempts were made to melt aluminum in the submerged-resistor furnace, designed for brass and other heavy metals, the resistor channels were clogged up by nonmetallic particles which adhered to the channel walls.

TABLE 79. OPERATING DATA OF ELECTRIC FURNACES FOR NONFERROUS MELTING

Characteristics	Detroit	Detroit	Detroit	Detroit	Ajax-Wyatt (75 kw.)	Ajax-Wyatt (75 kw.)	Ajax-Wyatt (75 kw.)	Ajax-Wyatt (60 kw.)	Ajax-Wyatt (60 kw.)
Material melted	Cu 85, Sn 5, Pb 5, Zn 5%	Cu 73, Sn 7, Pb 20%	Ni 23, Cu 69, Sn 5, Pb 1%	Gray iron borings	Cu 85, Sn 5, Pb 5, Zn 5%	Ni 18, Cu 65%	Pure Cu	Zinc	Cu 70, Pb 5, Zn 25%
Weight of charge, lb.	2,000	1,000	300	1,000	700– 800	700– 800	700– 800	900–1,000	800
Pouring temperature, deg. C.	1175–1200	1150–1200	1315	1590	1200–1250	1250–1290	1125–1175	435– 460	1125–1175
Average melting time, min.	50	40	30	60	70– 80	75– 85	75– 90	40– 45	60– 70
Power consumption, kw.-hr. per ton.	285	260	421	600	252	275– 290	210	90	190– 210
Electrode consumption, lb. per ton.	3.25	3.50	5	7					
Lining life, number of heats.	2,000	2,000	1,000–2,000	300–500	1,000	1,500	500	3,000	3,000
Metal loss, per cent.	0.5	0.7	. . . . . .	3	0.4	0 5–0.75	Nominal	0.25 dross	0.5–1.00

Figure 210 shows an induction furnace of the submerged-resistor type (Ajax-Tama) in which aluminum alloys can be melted continuously without fear of clogging the melting channels. The secondary circuit consists of two or more straight vertical channels connected at the bottom by a horizontal channel of larger cross section. Depending upon the kind of metal charged into the furnace, there will be some deposits of slags in the channels, chiefly in the vertical legs. However, these deposits
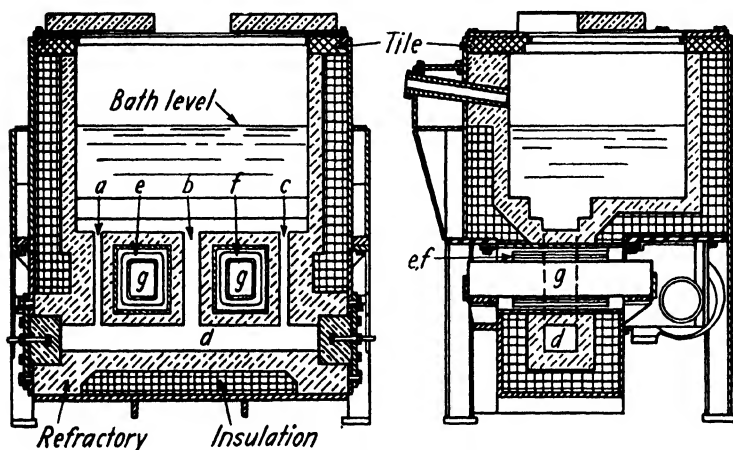
Fig. 210. Principal vertical sections of induction furnace for aluminum (Ajax-Tama). *a, b, c, d*, metal channels; *g*, primary coil with protections *e* and *f*.

can be easily scraped off from time to time by using tubular tools having the same cross section as the channels. The slag particles are scraped off and can in most cases be extracted from the surface of the metal.

Both the rocking and induction furnaces are efficient in energy consumption, show metal losses of less than 1 per cent during melting, and produce the necessary stirring action for homogeneous products. They have found different fields of application in that the induction furnace has been applied in rolling mills for melting brass of relatively low copper and lead content where production of the same type of metal of uniform analysis is continuously demanded. The rocking furnace is used for melting nonferrous alloys, including bronzes, high copper and lead brasses, nickel alloys, and cast iron, under either intermittent or continuous production demands.

Resistance Furnaces. During the early development of electric brass melting, resistor furnaces of the granular carbon resistor type, an example of which is the Baily furnace, found considerable application. It consisted of a vertical steel shell mounted on trunnions enclosing a shallow circular hearth, which in turn was surrounded with an annular refractory channel filled with granular carbon. The passage of the current through the resistor material generated heat which was radiated to the walls and roof of the chamber and reflected to the charge. The resistor consisted of broken carbon or graphite of $\frac{1}{4}$-in. mesh, and the refractory channel was of SiC or Carborundum firesand. A 105-kw furnace had a capacity of 1,500 lb of brass and operated on single-phase currents at 100 volts and 1,100 amp, at a power factor of about 98. Melting losses were 0.8 to 1 per cent. For charge loads such as those of 500 to 1,000 kw, rectangular stationary furnaces were built. The limitations of the Baily furnace were its low thermal efficiency, its lack of means for stirring the charge, its relative slowness of heating, as well as mechanical difficulties encountered in maintaining the refractory channel. In brass melting it is now obsolete, but the furnace design has been applied to units for heat-treatment of metals. Even in this case it has encountered severe opposition from resistor furnaces of other types.

Small-sized experimental furnaces capable of producing very high temperatures have been built on the resistor principle. A graphite electrode of small cross section is fixed in the upper part of a furnace cylinder or chamber and very high amperage currents pass through it, the graphite being heated almost to the volatilization point of carbon. The heat is reflected from the furnace walls onto the charge, and in certain designs is focused onto a small hearth.

Induction Furnaces, High Frequency. Electric power may be converted into heat by induction through the utilization of strong magnetic fields at low frequencies (60 cycles or less), or comparatively weak magnetic fields at relatively high frequencies (360 to 2,000 cycles per sec or higher). The strong magnetic field low frequency requires interlinkage of an iron core with the coil and with a loop or ring of the material to be heated in an arrangement corresponding to the core, primary, and secondary of a transformer. The use of high-frequency current

makes it possible to dispense entirely with the iron core and eliminates the necessity of looping the conductor which is to be heated. The same amount of heat may be created with a field of unit strength and a frequency of 6,000 cycles per sec as with a field 100 times as strong and a frequency of but 60 cycles per sec.

The best known high-frequency furnace is the coreless induction furnace invented by E. F. Northrup in 1916. Its principle is shown in Fig. 211. It is that of an air transformer whose primary is the furnace coil and whose secondary is the melt, or,
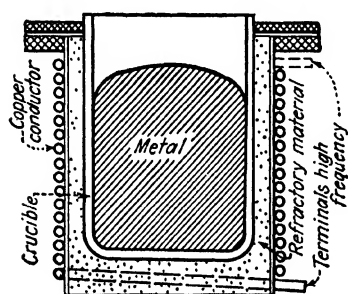
Fig. 211. Construction of Ajax-Northrup coreless induction furnace.

if the melt be nonconducting, a conducting crucible containing the melt. The primary is a helical coil of copper tubing through which water is passed for cooling purposes. This conductor is insulated both thermally and electrically from the crucible. When high-frequency currents are applied to the terminals of the copper helix, all the space inside the coil is subjected to a rapidly alternating electromagnetic field which induces currents in the furnace charge or conducting crucible. These induced currents cause rapid and efficient heating.

The thickness of the thermal insulation between the charge and the primary coil has a large bearing on thermal efficiency. The thicker it is, the less will be the proportion of electromagnetic energy to enter the heating chamber, while the thinner the insulation the greater will be the thermal energy radiated out from the crucible. Although insulation does not obstruct the electromagnetic field, the greater the space it occupies, the smaller becomes the portion of the field which cuts the charge. Ordinarily relatively little thermal insulation is needed, because high-frequency heating is extremely rapid and relatively little heat escapes by radiation.

In their early development, high-frequency furnaces were built in small sizes, and power was supplied to them by high-frequency oscillators consisting of a special type of step-up transformer with a suitable inherent reactance, a mercury discharge gap

chamber, and two separate banks of electrostatic condensers. The transformer primary was connected to a single-phase power supply, and the secondary was in series with the two banks of condensers through the furnace induction coil and in parallel with the discharge gap.   About 1925, commercially large and efficient high-frequency generators as well as satisfactory condensers became available for large units.   A typical wiring diagram for furnaces about 60 kw is shown in Fig. 212.   At the
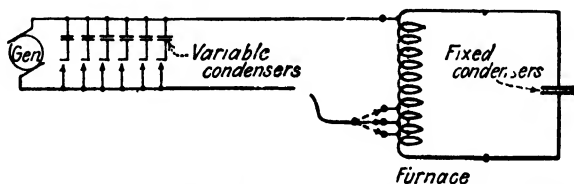
Fig. 212.   Wiring diagram of large Ajax-Northrup furnace.

present time units of 100 to 2,000 lb with generators of 60 to 600 kw are in use.   The melting times are from 35 min in the smaller size to 1 hr in the larger ones, at rates of 180 to 2,000 lb per hr and power consumptions of 1,000 kwhr per ton in the 100-lb furnace to 550 kwhr per ton in the 2,000-lb furnace. The field of application has been wide, covering nonferrous alloys, sterling silver, special steels, corrosion-resistant alloys, magnetic materials, and a large variety of experimentally produced metals.

The practical limits to the temperatures obtainable in the high-frequency furnaces are those imposed by the inability of the materials of construction to withstand the temperatures created. During melting, the electromagnetic forces tend to produce a stirring action on the charge, which is often quite violent in the case of conducting charges.   The heating efficiency of high-frequency apparatus increases with increase in capacity of the units employed.   Rates of heating may be as fast or slow as desired to satisfy the needs of any industrial operation.

CHAPTER 22

METALLIC ELECTROTHERMAL PRODUCTS

Ferroalloys. The demand for ferroalloys is governed to a large extent by the requirements of the iron and steel industry. Specifications for ordinary tool and alloy steels as well as castings have become more and more rigid, and the steelmakers must depend on ferroalloys to meet these requirements. A ferroalloy is an alloy of iron and some other metal or metals. It is used by the steelmakers for the introduction into steel of a definite percentage of the alloy metal to give the steel certain physical properties, depending upon the alloy used; or as a cleansing or deoxidizing agent, the alloy combining with the oxygen or oxides or other impurities and the reaction products passing off in the slag. With the development of engineering steels having special properties, of corrosion-resistant steels of the chromium-nickel type, of straight high-chromium alloys resistant to scaling and oxidation at high temperatures, of the high-silicon irons and a number of special alloys, increased demands have been made on the ferroalloy industry.

Prior to about 1890, ferroalloys were made in the blast furnace or crucible and to a limited extent in the open-hearth furnace. High-carbon ferromanganese and low-percentage manganese alloys such as spiegeleisen and silicon-spiegel, 15 per cent ferrosilicon, and some ferrophosphorus are still made by blast-furnace methods. These methods had their limitations in that the blast-furnace temperatures were not high enough for the reduction of some of the refractory oxides of the alloying metals, and low-carbon alloys could not be produced. The crucible method suffered the same limitations with the additional disadvantage of small tonnage. The introduction of the electric furnace was the active beginning of the ferroalloy industry on a commercial scale. A further development was caused by the crisis in the carbide industry between 1895 and 1900, when makers of this product, particularly in Europe, found their

capacity in excess of the demands for carbide and were forced to find other products to be made in the carbide furnaces.

The alloys in use for deoxidizing are ferromanganese, ferrosilicon, and to a smaller extent silicomanganese, ferroaluminum-silicon, silicon-zirconium, and ferrotitanium. Those used for imparting special properties to steel or for the formation of alloy steels are ferromanganese, ferrosilicon, ferrochromium, ferrotungsten, ferromolybdenum, ferrovanadium, and to a smaller extent ferrotitanium, ferrouranium, ferrophosphorus, silicon-zirconium, and other minor materials

Furnaces. The general design of electric furnaces for the production of alloys is much the same, but they differ in electrical connections, number and arrangement of electrodes, and shape and size of the hearth. The furnaces are single, two, or three phase. The simplest type is that of Siemens, in which current enters through a vertical electrode suspended in the furnace directly over the conducting hearth which serves as the other electrode. The furnace shell is usually cylindrical with a tap hole provided at the lower side. The electrode is raised or lowered either by hand or by a motor-operated winch connected to the electrode by a cable. This type is employed in the production of ferrotungsten and ferromolybdenum. When the alloys produced cannot be tapped, the furnace can be knocked down, and the alloy button removed.

In another modification of a single-phase furnace, two electrodes are used arranged vertically, the current passing through one electrode into the charge and out the other. The shell is usually rectangular, and the furnace is built with an open or closed top. Two-phase furnaces find little application. The three-phase furnace is used almost entirely for the production of ferromanganese, ferrosilicon, ferrochromium, and ferrovanadium. The shell is either rectangular or oval, lined with a refractory material; the bottom of the furnace is lined with carbon or carbon blocks. The furnace shell is of steel plate, is either air or water cooled, with a tap hole provided at the lower side. The units usually have open tops to permit continuous charging, save in the cases where volatilization losses are great enough to warrant totally enclosed furnaces equipped with mechanical charging devices.

The energy consumption for different alloys is dependent upon

the size of the furnace employed, the proper handling of the charge and the operations conducted, the percentage of the alloying metal, and the percentage of carbon in the product. The furnace voltage required for smelting ferroalloys usually ranges from 50 to 160, the most suitable voltage depending upon the general furnace layout. Multitap transformers capable of giving several different voltages are often employed so that different alloys can be made in the same furnace at different times.

Ferrosilicon. Ferrosilicon, in point of tonnage, is one of the most important of the ferroalloys. It is largely used for deoxidizing steel during refining, in the manufacture of steel castings, for the introduction of silicon into cast iron, and the production of high-silicon steel for electrical purposes and high-silicon iron for corrosion-resistant metals. It can be made in the blast furnace, in which case the silicon content seldom exceeds 15 per cent, while the products from the electric furnace range as high as 90 to 95 per cent Si. Ferrosilicons between 45 and 60 per cent Si show a tendency to disintegrate with the production of SiH_4 gas accompanied by PH_3 if impure raw materials be used. The phosphorus content of the ferrosilicon is very important. If phosphorus run high and be accompanied by a small amount of calcium exceeding certain limits, disintegration sets in. The common grades manufactured are 15 per cent, 50 per cent, 75 per cent, and 90 per cent ferrosilicons, whose approximate compositions are given in Table 80.

TABLE 80. ANALYSIS OF FERROSILICONS

Constituent	15 % ferrosilicon	50 % ferrosilicon	75 % ferrosilicon	90 % ferrosilicon
Percentage Si.....	14–16	47–52	75–79	90–94
Percentage Fe.. .	....	48	20	4.50
Percentage C.....	1 (max.)	0.1	0.1	0.1
Percentage P...	0.05 (max.)	0.05	0.05	0.05
Melting point, °C.	1280	1360	1360	1330–1450

The raw materials are silica in the form of quartzite or sand, iron as low-phosphorus, low-sulfur soft-iron and steel turnings or chips, and a carbonaceous reducing agent such as charcoal or high-grade coke low in sulfur and phosphorus. The chief impurities in the raw materials are Al_2O_3, MgO, and CaO, which

form the slag. The furnaces employed are of the mixed arc-resistance type with three vertical electrodes operating on three-phase current. A typical one is illustrated in Fig. 213. The furnace shell is of steel plate, air-cooled, with a refractory lining, on top of which is a carbonaceous layer. In operation a crust of

Fig. 213.   A 2,500-kva ferrosilicon furnace.   (*Southern Ferro Alloys Company.*)

solidified charge forms the working lining. Operating details are given in Table 81.

Silicon. The first attempts to make silicon employed a resistance furnace such as is used for SiC. Arc furnaces are now used, similar to those employed for the manufacture of high-percentage ferrosilicon. The raw material is silica rock and carbon. A typical three-phase 3,000-kw furnace operating at 120 volts is 14 ft long, 8 ft wide, and 5 ft deep. The furnaces are rectangular in section, being built of a steel shell lined with blocks of carbon. A 3,000-kw furnace produces about 5½ tons of 90 to 95 per cent silicon in 24 hr. When high-grade silica sand and petroleum coke or other reductants are used as raw materials, 95 to 97 per cent silicon may be made. The energy consumption is less than 6 kwhr per lb Si. The principal uses of silicon are as an alloying agent for light metals such as aluminum, a reducing

agent for the production of certain alloys of vanadium and chromium, particularly low-carbon ferroalloys containing these elements.   Typical commercial grades are:

	Maximum 1% Fe grade	Maximum 2% Fe grade	Maximum 3% Fe grade
Si	97% (min.)	96% (min.)	95% (min.)
Fe................ ..	1% (max.)	2% (max.)	3% (max.)

Ferromanganese.   Ferromanganese is employed as a deoxidizer and as an alloying constituent for the production of hard and tough steels containing 12 to 14 per cent Mn, and of a much larger tonnage of engineering steels having 1 to 2 per cent Mn. Spiegeleisen containing up to about 20 per cent Mn was for many years made only in the blast furnace, and a similar condition held true for the higher manganese alloys up to 70 to 80 per cent, in that it was thought that the volatilization losses in electric furnaces, as a function of the higher temperatures reached, would be prohibitive.   It was later discovered that in a well-designed, well-operated furnace these losses can be minimized. Actual smelting of the alloys is easier than in the blast furnace, slag loss is less, and low-carbon products, not producible in the blast, can be made in electric furnaces.   Spiegeleisen, used in bessemer and basic open-hearth practice, has an approximate chemical analysis of 15 to 30 per cent Mn, 4.5 to 5 per cent C, 1.00 per cent (max.) Si, 0.05 per cent S, 0.15 per cent P.   A standard grade of ferromanganese contains approximately Mn 78 to 82 per cent, Fe 15 to 19 per cent, C 6 to 8 per cent, Si 1.00 per cent (max.), P 0.35 per cent (max.), S 0.05 per cent (max.). A low-carbon ferromanganese, preferred for use in low-carbon steels, has an approximate composition of Mn 80 to 85 per cent, Si 1 per cent (max.), and C either 0.30 max. or 1 max. per cent.

The raw materials are manganese ores containing 45 to 50 per cent Mn, carbonaceous reducing agents, iron or iron ore, and suitable slag-forming materials if necessary, depending upon the constituents of the charge.   Ferromanganese furnaces are in general similar to those used for ferrosilicon, although they may be of the closed-top type with provision made for the collection and utilization of gaseous products from the furnace.   When

ferromanganese is made in the electric furnace, manganese recovery is ordinarily greater than when the product is made in the blast furnace, and lower carbon-content ferroalloys can be produced. Smaller amounts of flux are used in the electric furnace than in the blast furnace and losses of manganese in slags are lower, so that 90 per cent or better of the manganese content of the ores in electric-furnace operation can be obtained in the finished ferromanganese. Coke consumption in blast furnaces when ferromanganese is produced is more than double the coke consumption for the production of pig iron in the same unit. Typical operating data are given in Table 81.

Manganese. Manganese metal is produced in electric furnaces by silicon reduction of low iron-content manganese ores. It is used as an alloying agent for nonferrous alloys and for certain resistance wires. It is furnished in two grades, one analyzing Mn 96 to 97 per cent, Fe 2 per cent (max.), Si 1 per cent (max.), C 0.25 per cent (max.), and the other Mn 95 to 96 per cent, Fe 3 per cent (max.), Si 1 per cent (max.), C 0.25 per cent (max.). Electrolytic manganese (99.9+) is competitive.

Ferrochromium. Ferrochromium is used for the production of chromium steels which are exceedingly hard, useful for armor plate and projectiles. It is extensively employed in the manufacture of heat-resistant chromium alloys, chromium-nickel, chromium-molybdenum, chromium-vanadium, engineering, automotive, and tool steels, as well as for the corrosion-resistant alloys from 10 to 30 per cent Cr and those of the chromium-nickel variety such as the 18-chromium 8-nickel type. The material is produced chiefly as an alloy containing 65 to 75 per cent Cr, 4 to 8 per cent C, and 1 to 3 per cent Si, or in grades of lower carbon content. The grades known as maximum 5 per cent and maximum 6 per cent carbon constitute the bulk of the demand. The alloy is furnished either in lumps weighing as much as 75 lb or in crushed form. A typical analysis would show 66 to 70 per cent Cr and would be graded according to carbon content into classes 4 to 5, 5 to 6, or 6 to 7, with melting points from 1200 to 1300°C. The raw materials are chrome-iron ore, carbonaceous reducing agents, and the necessary slag-forming materials depending upon the charge constituents. The furnaces used are in general similar to those employed for ferrosilicon, but they differ materially in details.

Linings of the furnaces last from 1 to 3 years.   For a product of 4 to 6 per cent C, 66 to 70 per cent Cr, approximately 2.5 tons of 48 per cent Cr ore are needed per ton of ferroalloy.   Electrodes are often operated 2 ft deep in the charge.   Metallurgical efficiencies are 80 to 85 per cent.   Some typical operating data are included in Table 81.   Ferrochromium furnaces can be operated to give low-carbon products if desired, but only at the expense of increasing losses of chromium in the slags.   When an 8 per cent carbon product is made, 90 to 95 per cent of the chromium charge may be recovered as ferrochromium; but if 6 per cent carbon be produced, the chromium recovery is somewhat lower.   For the production of low-carbon ferrochromiums, silicon metal or high silicon-content ferrosilicons are employed as reducing agents instead of carbonaceous materials.   The low-carbon ferrochromiums show typical analyses of 67 to 72 per cent Cr in grades according to carbon content of 0.06, 0.1, 0.2, 0.3, 0.5, 1, and 2 per cent, with a maximum of 1 per cent Si. The melting point ranges from 1370 to 1550°C.

Chromium.   Chromium metal is produced by the silicon reduction of chromium ores in electric furnaces, the product being used for nonscaling alloys subjected to high temperatures, resistance wires, and alloys for electrical heating appliances, as well as for some special corrosion-resistant alloys.   It is furnished in two grades, one running 97 to 98 per cent Cr with a maximum of 1 per cent Fe, another with 96 to 97 per cent Cr with a maximum of 1.5 per cent Fe, with carbon contents of either 0.2 or 0.5.

Ferrotungsten.   Ferrotungsten is used for the manufacture of high-speed tool steels and other alloys.   Only those low in W can be tapped readily, because of the high melting point of the alloys.   The raw materials are tungsten minerals such as wolframite [$(Fe, Mn)WO_4$], ferberite ($FeWO_4$), and scheelite ($CaWO_4$); carbonaceous fuel; slagging materials; and iron ore or scrap iron.   The practice is to use small furnaces worked intermittently, which are dismantled at the end of every run and the solid block of alloy is taken out.   Ferrotungsten takes up carbon but to a lesser degree than does ferrochromium.   The most common grade is 78 to 83 per cent W, 0.75 per cent Si (max.), and 1.00 per cent C (max.), with a melting point of approximately 1800 to 1900°C.   Some operating data are given in Table 81.

Ferromolybdenum. Ferromolybdenum is used for alloys such as the engineering, aircraft, and automotive steels and for ferrous metals for a number of special purposes, often in connection with other metals. The raw materials are in some cases roasted molybdenum concentrates such as molybdenite (MoS_2) or molybdenum sulfide directly, iron or steel scrap and turnings, carbonaceous or metallic (Si) reductants, and lime. Alloys up to 50 or 60 per cent Mo can be tapped, but those above this percentage are manufactured in a manner similar to that used for ferrotungsten. Typical operating data are given in Table 81. The most common grade is Mo 50 to 60 per cent, S under 0.25 per cent, Si 1.50 per cent, low-carbon grade 0.25 per cent C, high-carbon grade 2 per cent C. In recent years calcium molybdate ($CaMoO_4$) has been replacing ferromolybdenum in the production of molybdenum steels. It has the advantage of being practically a carbon-free material. Its composition is approximately 40 per cent Mo and 25 per cent CaO.

Ferrovanadium. Ferrovanadium imparts to steel the property of resisting shock and vibration, being used for vanadium and other alloy steels. The raw materials are vanadium ore concentrates high in V_2O_5 which are smelted with iron and fluxes, with reducing agents such as coke, 90 to 95 per cent silicon or ferrosilicon. Relatively high temperatures of reduction are needed, at which point vanadium shows considerable chemical activity. Furnaces have a very small hearth for the power input and are of such design that the alloy immediately leaves the electrode zone. The furnaces consist of cast-iron shells lined with refractory, inside of which is a tamped graphite and carbon block hearth. The furnace is totally enclosed, electrodes passing vertically through the roof, with tap and slag holes located in one side in the front. A typical furnace is shown in Fig. 214. The mixed and pulverized charge, consisting of ore, reducing agents, and fluxes, is delivered automatically into the electrode zone. Furnace arcs are maintained below the slag layer into which the electrodes dip. A typical furnace construction is shown in Fig. 215. The furnaces are three phase, operating at full load at 220 volts, power factors being above 95 per cent. A typical product is 33 to 42 per cent V, 3 to 5 per cent Si, 0.5 to 3 per cent C. Another is 35 to 40 per cent V, 8 to 12 per cent Si, 2 to 3 per cent C; although other grades containing higher
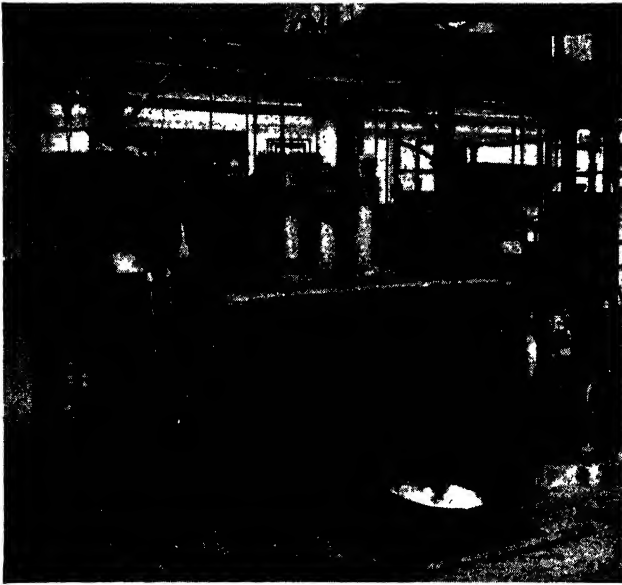
FIG. 214. A ferrovanadium furnace. (*Vanadium Corporation of America.*)
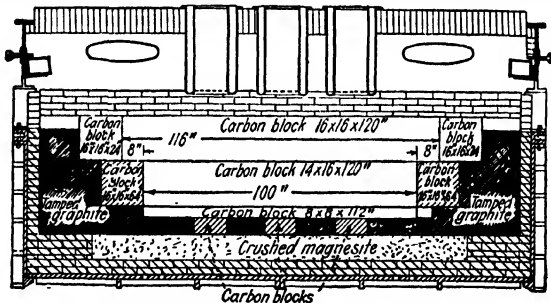
FIG. 215. Construction of ferrovanadium furnace. (*Vanadium Corporation of America.*)

vanadium, less silicon, and less carbon are produced. Ferrovanadium has a melting point between 1250 and 1400°C. Typical operating data are given in Table 81.

Silicomanganese. Silicomanganese has the advantages of both ferrosilicon and ferromanganese. It is employed for deoxidation and imparting favorable mechanical properties,

particularly with high-sulfur steels. It ordinarily has a lower carbon content than ferromanganese. It is produced in several grades whose compositions are approximately as follows:

Constituent	(1)	(2)
Percentage Mn....	65–70	65–70
Percentage Si........ . .	20–25	16–20
Percentage C, max. .	1.00	2 00

It can be made by the separate production of ferrosilicon and ferromanganese, which in their fluid condition are mixed together, when the carbon of the ferromanganese is precipitated as graphite which can be removed from the surface of the cooled alloy. It is more usually made in ferrosilicon furnaces from charges of siliceous manganese ore with scrap iron or steel and carbonaceous fuel, silica being added if necessary. Typical operating data are given in Table 81

Zirconium Alloys. Zirconium-ferrosilicons and silicon-zirconium are made in the electric furnace from zirconium silicates and zircon with carbon reductants. Zirconium-ferrosilicon is used in the same manner and as a substitute for ferrosilicon but yields sounder and cleaner metal. A typical grade is Zr 9 to 12 per cent, Si 40 to 47 per cent, Fe 40 to 45 per cent, C 0.20 per cent (max.). Silicon-zirconium is employed as a deoxidizer and scavenger. Zirconium has a beneficial effect on the hot working properties of high-sulfur steels. A typical grade is Zr 35 to 40 per cent, Si 47 to 52 per cent, Fe 6 to 10 per cent, C 0.50 per cent (max.).

Minor Alloys. *Calcium-silicon* is an electric-furnace product made from lime, silica, and a carbonaceous reducing agent. It is useful as a steel deoxidizer, owing to its ability to form a calcium silicate having a low melting point. It is manufactured in two grades according to iron content, the high iron being Ca 22 to 28 per cent, Si 65 to 70 per cent, Fe 5 per cent (max.), and the low iron being Ca 30 to 35 per cent, Si 60 per cent, Fe 3.5 per cent (max.).

Ferrosilicotitanium, useful as a steel deoxidizer, is made as a by-product of the Hoopes-Hall electric-furnace process for the refining of bauxite and the production of alumina.

TABLE 81. FERROALLOYS

Operation details	Ferrosilicon	Ferromanganese	Ferrochromium	Ferromolybdenum	Ferrotungsten	Ferrovanadium	Silicomanganese
Raw materials	SiO_2, C, and Fe	Mn ore, C, CaO, Fe ore or scrap steel	Chromite, coke, Fe ore or Fe	Molybdenite, Fe, C, and CaO	Tungsten ore, Fe ore or Fe, C, SiO_2	Vanadium ore, C, Fe, ferrosilicon or Si and fluxes	Mn ore, SiO_2, Fe, C
Furnace:							
Type	Arc resistance, 3-phase	Arc resistance, 3-phase	Arc resistance, 3-phase	Arc resistance, 1- and 3-phase	Arc resistance, 1-phase	Arc resistance, 1- and 3-phase	Arc resistance
Capacity, kw	4,000–12,000	3,500–9,000	1,500–5,000	200–750	500–750	2,000–4,000	4,000–8,000
Voltage	75–150	90–115	90–120	50–150	90–120	150–250	90–120
C.d. electrodes, amp/sq in	30–60	40–50	40–60				30–60
Energy consumption, kwhr/lb	2–2.5 (15% Si), 2–3.5 (50% Si), 3–3.5 (75% Si)	2–2.5 (75% Mn), 3–3.5 (80% Mn)	2–3, 3–3.5 (60% Cr), 3–4 (70% Cr)	3–4 (50% Mo), 4.5 (70% Mo)	Smelting 2.1, refining 1.7, total 3.8	2.3–4 (35–45% V)	2–3 (70% Mn)
Losses, %	10–15	10–20	7–10 (8% C)	10–20	8–10	10–25	15–25 Mn, 10–20 Si
Electrode consumption, lb/ton	25–50 (15% Si), 50–75 (50% Si), 80–120 (80% Si), 150–130 (90–95% Si)	70–100	50–70			......	80–120

Among other ferroalloys that should be mentioned is *ferro-titanium*, generally made in the electric furnace and to a smaller extent by the aluminothermic reduction process. The electric-furnace product contains about 16 per cent Ti and 7 per cent C. *Ferrophosphorus*, usually a blast-furnace product used in making sheet steel and for imparting free-cutting properties to steel pipe, is produced to a considerable extent in the electric furnace. *Ferrouranium*, 35 to 50 per cent U and 3 to 4 per cent C, is produced in small amounts in the electric furnace at an energy consumption of 3.5 kwhr per lb with a 75 per cent recovery of uranium. The deoxidizer *ferrosilicon-aluminum* is made by adding molten aluminum to ferrosilicon.

Electrothermic Zinc. The Cowles Brothers in 1885 proposed the use of the electric furnace for the smelting of zinc ores. DeLaval experimented in the field in 1893 and in 1898 had an intermittent operating furnace at Trollhättan in Sweden. Commercial furnaces were built during the years following in sizes of 350 and 500 hp, all being single phase with bottom hearth contact and one movable top electrode. Landis[1] has described the process in its later stages of development and furnaces with larger hearths and two top electrodes, one of which was suspended in the furnace and lowered as it was consumed and the other raised or lowered to control the power of the furnace. Lead and zinc were volatilized out of the smelting zone at temperatures above 1400°C and left as vapors mixed with CO_2 passing to water-cooled condensers, where the metals were recovered partly as liquid and partly as powder. The powder was sent to a rotary electric furnace for conversion into the liquid form, liquated, and cast. Power consumption per ton of 57 per cent Zn ore was of the order of 3,400 kwhr, or 6,600 kwhr per ton of zinc. Smelting alone consumed 2,150 kwhr per ton of ore.

O'Harra[2] reviewed the history of electrothermic zinc and compared the economics of the method with electrowinning and pyrometallurgy. The first cost of plant and greater adaptability to small-scale operations as compared to hydrometallurgy or electrowinning processes, along with the efficient utilization of energy by the electric furnace, are listed as advantages.

[1] Landis, W. S., *Trans. Am. Inst. Mining Met. Engrs.*, **121**, 573 (1936).
[2] O'Harra, B. M., *U.S. Bur. Mines, Bull.* 208, 106 pp. (1923).

Weaton[3,4] and Long[4] have described the direct production of metallic zinc by the electrothermic process. The furnaces are tall shafts 30 to 40 ft in over all height, with an inside diameter of 57 to 69 in. They are of the charge-resistor type where the charge serves as the current-carrying medium between two sets of electrodes, three in each set, spaced 24 ft apart vertically and 120 deg to each other horizontally. Operating conditions are given in Table 82. Diagrammatic representation of the furnace and condensers is shown in Fig. 216. Zinc is distilled out of the
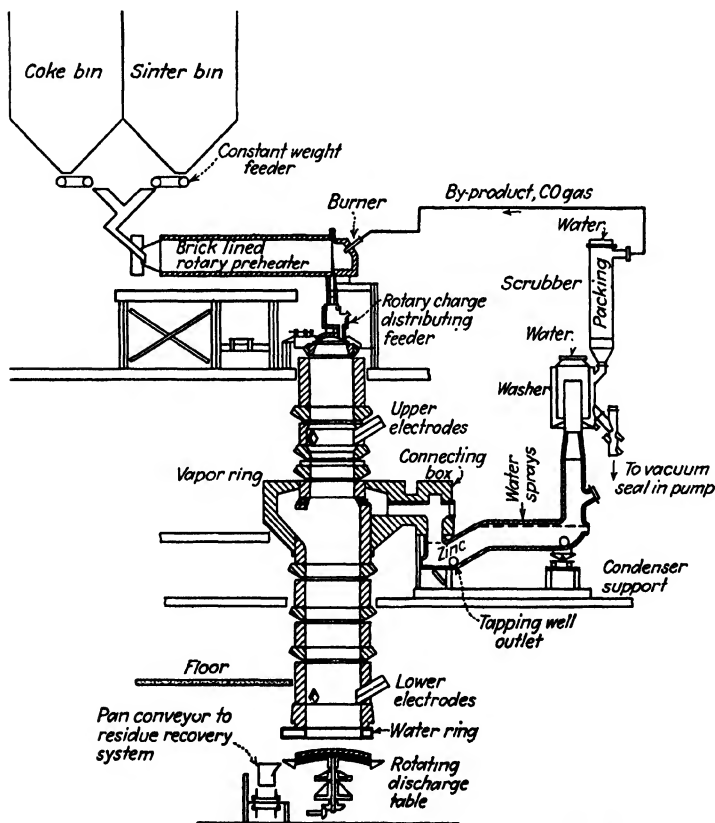
Fig. 216. Furnace and condensers for electrothermic zinc.

[3] WEATON, G. F., *Trans. Am. Inst. Mining Met. Engrs.*, **121**, 599 (1936).
[4] WEATON, G. F., and LONG, C. C., *Am. Inst. Mining Met. Engrs.*, *Tech. Pub.* 1040; *Metals Tech.*, **6**, February, 1939.

ore and condensed continuously, while the tapping and casting of the condensate are intermittent. Zinc in the form of finely divided metallic powder (blue powder) is collected in scrubbers and washers, dried, and returned directly to the furnaces. The zinc contains less than 0.007 per cent Fe or 0.025 per cent Pb.

Modification of the process involving the introduction of air into the furnace and the oxidation of the zinc vapors to zinc oxide results in an electrothermic production of this pigment. The zinc oxide is recovered in cyclone dust collectors and bag filters.

TABLE 82. ELECTROTHERMIC ZINC

Raw material.. .	Zinc sulfide concentrate analyzing Zn 58.28, Pb 0.56, insoluble 1.6, SiO. 1.12, Fe 6.4, CaO 0.47, MgO 0.27, S 31.9, Cd 0.1, Cu 0.06, Mn 0 24%
Charge ..	36 parts sinter, 16 parts coke
Furnaces:	
Capacity per day, tons of charge..	40
Size.... . .	37 ft high, inside diameter 57–69 in.
Power, kw.	1,500
Type..	Charge resistor
Temperature, °C.	Core 1400, main body 1200
Electrodes:	
Number...	2 sets of 3 each
Spacing.	24 ft apart vertically, 120-deg angle horizontally
Material .. .	Pitch-impregnated carbon
Size.....	60–72 in. long, 12 in. square
Consumption, lb/ton of metal produced... .	5
Energy consumption, kwhr/ton of Zn.	2,564
Amperes per electrode....... ...	1,800–2,000
Voltage of furnace..................	250–275

CHAPTER 23

CALCIUM CARBIDE AND CYANAMIDE

Calcium carbide is produced in the electric furnace according to the reaction

$$CaO + 3C \rightleftharpoons CaC_2 + CO - 108{,}000 \text{ cal}^1$$
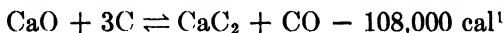
which is endothermic and reversible. At high temperatures the reaction proceeds from left to right, while at low temperatures the equilibrium moves in favor of the left-hand side of the equation. The reaction according to the phase rule has one degree of freedom; *i.e.*, at any given temperature one definite pressure of CO corresponds to equilibrium. At 1475°C the equilibrium CO pressure is 0.82 mm Hg. Thompson[2] states that above 1500°C CaC_2 decomposes into its elements but not so rapidly as it is produced; otherwise its manufacture would not be possible.

Raw Materials. The raw materials for carbide manufacture are lime and carbon which must be available in commercial quantities and of purities obtainable at economic costs. Relatively large quantities of impurities result in either thick crusts in small furnaces, or the building up of crusty and partly solidified portions of the charge between electrodes in large furnaces. As such, the impurities are objectionable in that they interfere with regular and effective operation of the furnaces. The impurities consume power for bringing them up to the furnace temperature and for their elimination. The lime must be of good quality chemically as well as have mechanical strength, without tendency to crumble into dust. In the United States carbonaceous materials are coke and, if economically available, charcoal, while in Europe anthracite coal is also employed. Charcoal is usually

---

[1] BRINER, E., and KUHNE, A., *J. chim. phys.*, **12**, 432 (1914), give 110,000 cal, while the Report on Fixation and Utilization of Nitrogen (1922) of the U.S. Fixed Nitrogen Research Laboratory gives 105,000 cal.

[2] THOMPSON, M. DE K., *Proc. Am. Acad.*, **45**, 431 (1910); *Met. & Chem. Eng.*, **4**, 327 (1910).

more expensive, is light and brittle, is low in fixed carbon, and has a high resistance. Its use gives the purest carbide and allows easy operation of the furnace. Even as little as 20 per cent of the carbonaceous charge in the form of charcoal markedly betters furnace-operating conditions. Petroleum coke, a pure form of carbon available in large quantities, finds considerable employment, although it is more expensive than coal or coke. In the United States coke is almost universally used. It is desirable to obtain these materials with as low ash, moisture, sulfur, and phosphorus as possible. The principal disadvantages of coke are its high ash, which should not exceed 12 and is usually around 8 per cent, and its moisture, which is of the order of 6 per cent; but the coke is always dried before use. It has the advantage that the furnaces start more easily and work with less trouble than with anthracite. Coal has a slightly higher fixed carbon percentage than coke and a lower ash, the value of which is around 4 per cent. It may contain iron pyrites, which causes the formation of ferrosilicon from the silica in the lime. In ingot furnaces the ferrosilicon remains distributed throughout the carbide, but in tapping units it collects at the bottom of the hearth and from time to time runs out with the tapped carbide. When ingot furnaces were operated, the ferrosilicon was removed from the crushed carbide by magnetic separation and hand picking. This is done to a slight extent in the case of carbide from tapping furnaces.

Phosphorus in the carbonaceous materials is a most serious impurity, as, in the strongly reducing conditions of the furnace, it will appear in the product as a phosphide which, when water is used to convert the carbide into acetylene, will liberate poisonous PH_3. When acetylene from phosphorus-containing carbide is burned, a haze of phosphoric acid appears around the burner. Sulfur is not usually a serious impurity, in that it is partly volatilized in the furnace. With present methods of acetylene generation in which large volumes of water are used, sulfur impurities under ordinary conditions of the carbide are not important.

The purity and physical properties of limestone are important in determining its fitness for carbide manufacture. When it is burned to lime, it loses nearly half its weight with the consequent increase to almost double the amount of impurities. Limestone

suitable for carbide should be at least 97 per cent $CaCO_3$. As much as 1 per cent MgO may be present, but it interferes with furnace operation, consumes power, and lowers production, although it is almost entirely volatilized during furnace operation. Alumina impurities interfere with CaC_2 formation, consume power, and lower production. Silica in the limestone lowers the fusion temperature in the furnace so that the quantity of tapped material is increased, but the product generally contains a lower percentage of CaC_2. Inasmuch as the carbide operator is essentially interested not in total tonnage but in total quantity of CaC_2, silica is an interfering impurity, particularly if there be as much as 2 per cent in the limestone and the magnesia content be also high. Silica in the limestone, if iron or iron oxides be very deficient, does not readily form ferrosilicon. If there be sufficient iron, the silica will be reduced. Bingham[3] gives as a desirable limestone for carbide manufacture one having the following maximum quantities of impurities: MgO 0.5 per cent, Al_2O_3 and Fe_2O_3 0.5 per cent, P 0.004 per cent, SiO_2 1.2 per cent, S traces only. Limestone of such quality is not readily obtainable in very large tonnages required for the carbide business.

Furnace Types. Calcium carbide is made in smothered arc furnaces from which it is removed either as a solid ingot or by tapping while in molten form. The electrodes are deeply buried in the charge and arcs exist only around the tips of the electrodes between the electrode and the surrounding charge. The ingot furnaces, now obsolete, may be subdivided into the intermittent and continuous types. They will be included in this discussion because of their historical importance, inasmuch as formerly they were the foundation of the carbide business. The tapping furnaces are large in size. The furnaces are fundamentally simple in design; because of their capacity and high power consumption, however, they have become complicated mechanisms. Present-day units are equipped with mechanical charging and tapping devices, apparatus for the removal of gases, large-size electrodes, and means of electrode regulation. The large power requirements for the furnaces, particularly because of their high-current nature, necessitate special electrical equipment. Supporting of the large electrodes and making the necessary

[3] BINGHAM, C., "Manufacture of Carbide of Calcium," W. Wesley and Son, London, 1920.

current contacts to them have brought about the development of relatively complicated electrode holders and methods of joining electrodes for continuous feed.

Ingot Furnaces. The original ingot furnace consisted of a carbon-lined steel box on wheels. The bottom of the lining served as a hearth electrode to which an arc was sprung from another mounted vertically. The box or furnace shell had a refractory-lined, funnel-shaped, sheet-iron extension into which the charge was shoveled and heaped around the electrode. During the run the upper electrode was gradually raised manually
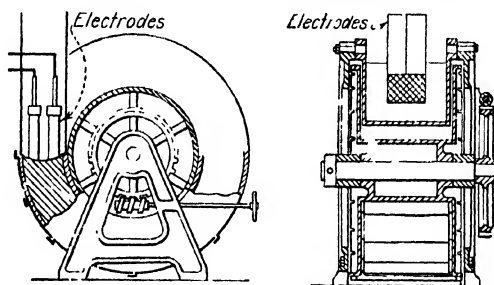
FIG. 217. Horry furnace.

as the carbide was formed in the furnace. When the box was filled, the current was cut off. The car was disconnected and removed. After cooling, the block or ingot formed was lifted out, freed of unreacted charge, broken up, and packed. The discontinuous ingot furnaces are obsolete. They had low energy efficiency, high consumption of raw materials, high labor charges, and small output.

Continuous ingot furnaces were developed to overcome the disadvantages of the intermittent type. The best known is that of Horry, the construction of which is shown in Fig. 217. It consisted of two vertical iron disks 8 ft in diameter and held 3 ft apart by a horizontal cylinder through which ran the shaft or axis of the furnace. An annular space was formed between this cylinder and a number of segmental cast-iron plates about 1 ft long whose sides were fastened to the circumference of the vertical disks. In practice only those segments necessary to make the bottom half of the furnace were used, the upper half being open. The electrodes projected vertically into the annular space through a shaft set tangentially, the charge being fed into

the shaft so that the electrodes were completely embedded. As carbide formed, it was removed from the electrode area by rotation of the unit and was taken off at a point diametrically opposite the electrodes. The furnace was slowly revolved, making a complete revolution in $1\frac{1}{2}$ days at a current of 4,000 amp at 75 to 80 volts. The entire operation of the furnace was automatic as far as electrode regulation, power feed, and rotation were concerned. The charge adjacent to the plates was not

Fig. 218.   Horry furnaces, electrode side.   (*Union Carbide Company.*)

fused, so that the actual working lining of the furnace was unreacted charge. The circular segment of fused carbide which did not stick to the furnace plate was removed from the furnace at the side opposite the electrodes. In operation, the outer segmental plates which formed the annular space were bolted on at a point near the electrodes and taken off at the opposite side. A typical installation of Horry furnaces is shown in Figs. 218 and 219.

Tapping Furnaces. Modern carbide furnaces are always of the tapping type. In the United States they are usually three phase three electrode; in Europe there has been an extensive development of single-phase hearth-electrode types of large capacity. A typical unit is shown in Fig. 220. In the three-

FIG. 219. Horry furnaces, discharge side. (*Union Carbide Company.*)
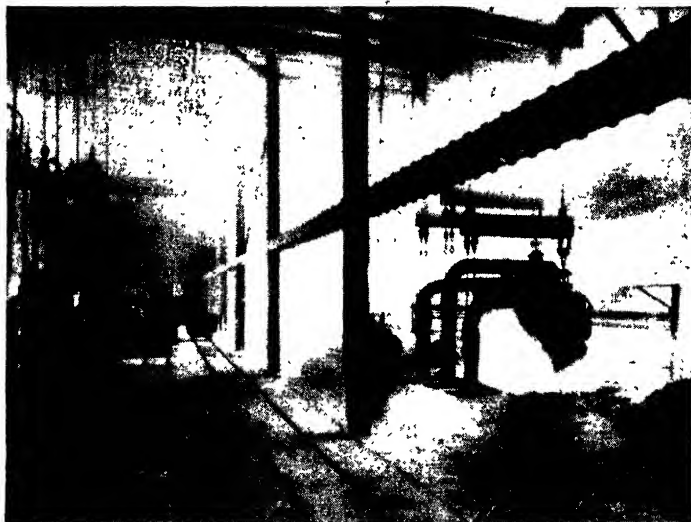
FIG. 220. Small carbide furnaces. (*American Cyanamid Co.*)

phase furnaces the electrodes are generally arranged vertically in line, whereas in some of the more recent ones they are located at the points of a triangle. Tapping holes are located in front of the furnace. In American practice there is usually one taphole per furnace. In continental units there may be as many tapholes

as there are electrodes. When this construction is employed in American units, tapping is done from only one taphole. The furnace itself consists of a rectangular boiler-plate shell, lined with refractory material which is in turn lined with carbon. The furnace linings are located far enough away from the electrodes so that they are not attacked by the high temperature or by the charge. Depending upon the power to the electrodes, no car-

Fig. 221. A German 7,000-kw carbide furnace. (*M. Sem.*)

bide is produced beyond a 1- to 3-ft radius. Heating is by smothered arcs between the electrodes, the hearth being electrically neutral. Electrical connection of the electrodes is ordinarily three-phase delta, although the star connection, with the hearth connected to the central point of the transformer, may be used. In operation, the furnace is really a smothered arc-resistance type, in that heating is done by arcs between the tips of the buried electrodes and the charge, and by resistance heating through the charge between the electrodes. Modern furnaces are continuously charged and tapped. Figure 221 shows the top of a 7,000-kw rectangular furnace, employing Söderberg electrodes. Operating characteristics of a small Italian plant are given in Table 83.

Currents of 25,000 to 40,000 amp per electrode or electrode bundle are normal, and American practice tends constantly to increase the current per electrode unit. Currents as high as

TABLE 83. OPERATING CHARACTERISTICS OF CALCIUM CARBIDE PLANT[1]

Furnace rating, kw	2,000
Furnace shape.	Elliptical
Electrodes:	
Size	20″ diam. × 21′8″
Number	3
Type.	Carbon, Söderberg
Phases.	3
Frequency	50
Electrode voltage...	55–95
Total amperage.........	24,000–50,000
Charge, kg	CaO, 970; coke, 300; charcoal, 330
Energy consumption per ton CaC_2, kwhr	3,300

[1] ZULIANI, G., *J. four élec.*, **56**, No. 2, 22–23 (1947).

240,000 amp per electrode bundle have been used in single-phase furnaces. It is stated that furnace voltages are 110 to 120 for units of the order of 3,500 to 4,000 kw, 130 for 7,000 to 7,500 kw, and 150 for 15,000 kw. Electrode current densities in single-phase furnaces are of the order of 20 to 22 amp per sq in. (3.1 to 3.4 amp per cm²) cross section, and 35 to 40 amp per sq in. (5.4 to 6.2 amp per cm²) in three-phase units.

Tapping furnaces may be classified as open or closed top, in the latter case the furnace gases and dust being collected and used. In operation the units are fed at the top, generally by automatic means, in a continuous or intermittent manner depending upon the size of the furnace, and tapped with the production of molten carbide through tapholes at the front of the furnace hearth. The molten material is run into either cast-iron chills, as shown in Fig. 222, or large saucerlike molds. The carbide is allowed to cool, is removed from the chills, and is broken up.

Miguet Furnace. In Europe the Miguet furnace for carbide has found considerable application. The hearth of the furnace is supported by pillars, enclosing a space for the transformers supplying the power. Forced air cooling of these transformers also cools the under part of the furnace and the interlaced conductors. The bottom of the furnace is made of two super-imposed thick plates of carbon which are divided into sections or blocks cemented together with carbon paste. The lowest part

of the lateral walls in contact with molten metal is also made of carbon. The furnace design enables the current to be led to a single electrode through a number of separate circuits symmetrically arranged around the furnace. The current in each of these circuits is relatively small, but the total may be as high as 240,000 amp. Details of design to increase the power factor make such high current capacity possible.

A large cross section of electrode is required for the high current capacity. The Miguet electrode is built by piecing together

Fig. 222.   Carbide chills.   (*American Cyanamid Company.*)

prebaked carbon segments, dovetailing the ends of these, and by bolting the segments together in the horizontal axis. The rigid electrode is supported by the bronze contact plates conducting the current to the electrode, the pressure of the plates being regulated by a mechanical arrangement. These plates are surrounded and held in place by a steel ring fastened to the four vertical suspension rods or cables. To lower the electrodes, pressure on the plates is released. The lowering is controlled by limiting spring stops which, when released after the electrode is in its new position, spring back to normal position.

All the supporting parts, the plates, ring, etc., are protected against gas fumes by a shield consisting of a water-cooled bronze circular casting around the electrode. This shield also acts as a current equalizer, since it is connected to the busbars on the out-

side and to the electrode contact plates by means of flexible laminated copper bars.

In order to add and to assemble the new electrode segments or blocks, a platform is provided directly above the furnace. This platform is cool and free from fumes, since the hot furnace gases are collected, cooled, and drawn out through ducts surrounding the electrode of the furnace and into a stack.

A 5,000-kw unit shows an energy consumption of 3,100 kwhr per metric ton of 80 per cent carbide. The Miguet electrode has been used for currents as high as 240,000 amp, in which case the electrode diameter is close to 10 ft, operating at current density of 21.1 amp per sq in. (3.25 amp per cm²) cross section.

Figure 223 diagrammatically illustrates the complexity of a modern carbide furnace of the single-phase single-electrode type. The furnace hearth constitutes only a small and simple part of the complete unit, while the complexity is due to charging arrangement, poking mechanism, electrode contacts, sectional electrodes, electrode supports, hangings and adjustments, as well as gas and dust offtakes and their accompanying blowers and collecting systems.

Energy Consumption and Distribution. Typical European operating data[4] show materials of a charge in the proportion of 980 lb of lime, 650 of coke, and 20 of electrodes from which 1,000 lb of 85 per cent carbide is produced. American practice uses a smaller percentage of coke. Table 84 shows the analysis

TABLE 84. ANALYSIS OF RAW MATERIALS FOR CARBIDE

Constituent	Lime	Coke	CaC$_2$	Electrodes
CaC$_2$.................	.....	.....	85.50	
C....................	.....	92.85	2.20	100
CaO...:..............	98.93	.....	8.25	
MgO.................	0.51	.....	0.40	
SiO$_2$.................	0.35	5.96	3.20	
S....................	.....	0.42	0.27	
Fe$_2$O$_3$ + Al$_2$O$_3$........	0.20	....	0.18	
H....................	.....	0.16	.....	
O....................	.....	0.33	.....	
N....................	.....	0.28	.....	

[4] BINGHAM, *op. cit.;* TAUSSIG, R., "Die Industrie des Kalziumkarbides," W. Knapp, Halle, 1930.
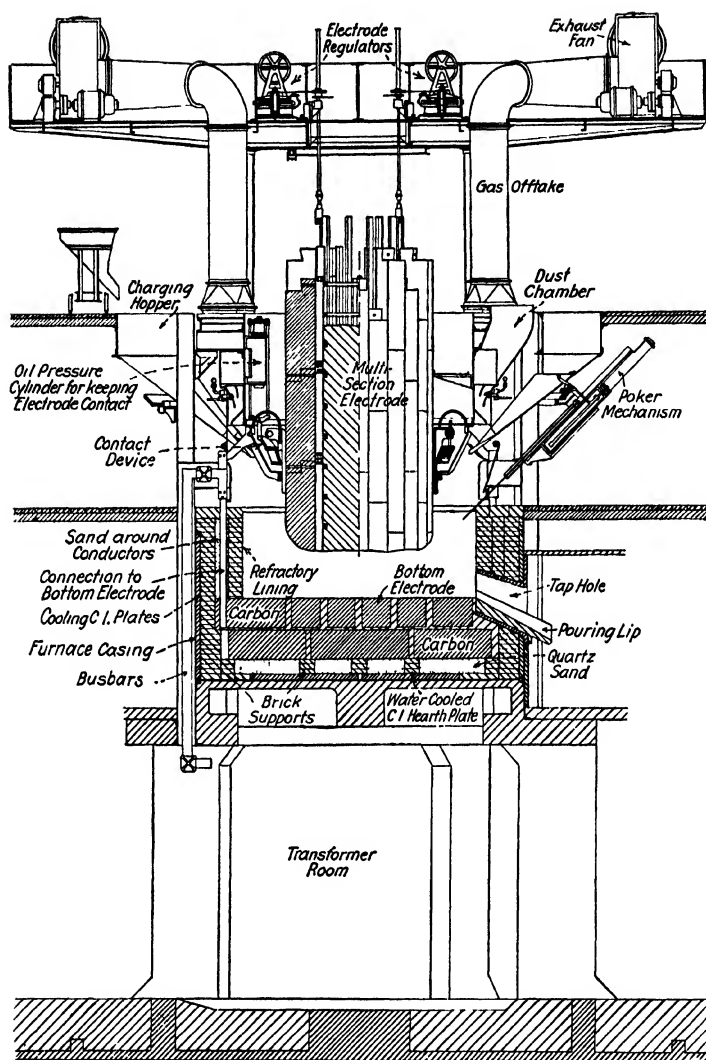
FIG. 223. Diagram of a large carbide furnace.

of the different portions of the charge, and in Table 85 the distribution of the various constituents of the raw materials is calculated.[5] A typical utilization of the·calcium content of the

TABLE 85.   DISTRIBUTION OF RAW MATERIAL CONSTITUENTS
(In pounds)

Constituent	Lime	Coke	Electrodes	Total	CaC₂	Dust	Gas
C......................	......	603.50	20	623.50	342.6	89	191.9
Ca.................	692.50	......	....	692.50	593.3	99.2	
O...................	279	2.1	...	281.1	25.2	.....	255.9
H...................	......	1.1	...	1.1	......	.....	1.1
N...................	......	1.8	...	1.8	......	.....	1.8
Mg................	3.0	......	....	3.0	2.4	0.6	
S...................	......	2.7	...	2.7	2.7	....	
Fe₂O₃ + Al₂O₃......	2.0	......	....	2.0	1.8	0.2	
SiO₂...............	3.5	38.8	....	42.3	32.0	10.3	
Total...........	980.0	650.0	20.0	1,650.0	1,000.0	199.3	450.7

lime and carbon of the coke is given in Figs. 224 and 225.   An energy distribution, based on the heat balance of a furnace whose energy consumption is 325 kwhr per 100 kg of 85 per cent carbide, or 3,250 kwhr per metric ton, or approximately
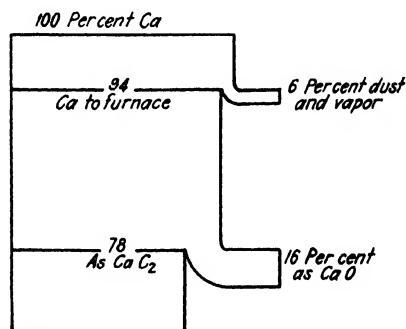
FIG. 224.   Utilization of calcium content of lime.

2,920 kwhr per short ton, is shown in Fig. 226.   On the basis of these figures, the energy for 1 metric ton of 100 per cent carbide would calculate to 3,830 kwhr.   If the heat of reaction for the

[5] SCHLUMBERGER, E., *Z. angew. Chem.*, **40**, 141 (1927).

formation of CaC_2 be taken as 108,000 cal, the theoretical energy for the production of 1 metric ton of 100 per cent CaC_2 would be approximately 1,940 kwhr. The energy efficiency for the formation of carbide would then be 1,940 divided by 3,830, or approximately 51 per cent. The heat of reaction used in these calculations is at room temperature. If the necessary energy be
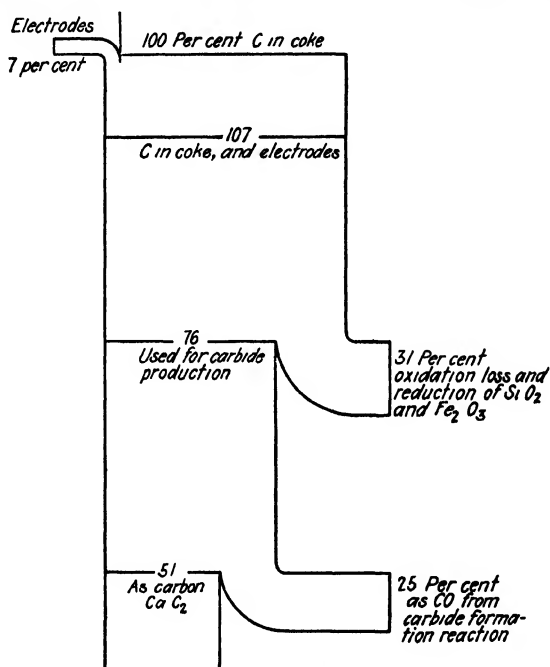
FIG. 225.   Utilization of carbon content of coke.

added for heating the carbide from room temperature to the temperature of tapping (2000°C) plus the necessary energy for heating the CO to 2000°, but crediting the operation with the sensible heat of the CO from the temperature at which it is formed to the temperature at which it leaves the furnace (800°), adding the latent heat of fusion of the .CaC_2 and the necessary heat consumed due to volatilization of calcium as well as the heating of the lime found in the final product from room temperature to 2000°, a figure of 2,530 kwhr per metric ton of 85 per cent carbide will be obtained. Using this as a theoretical energy figure against an actual energy consumption of 3,250, the energy efficiency calculates to 80 per cent.

Electrode consumptions are of the order of 2 to 4 per cent, being given as 20 to 40 kg per metric ton, or 40 to 60 lb per short ton of 85 per cent carbide.

Before the First World War, a furnace of 10,000 to 15,000 kva was considered large. They have grown to 25,000 kva or over.
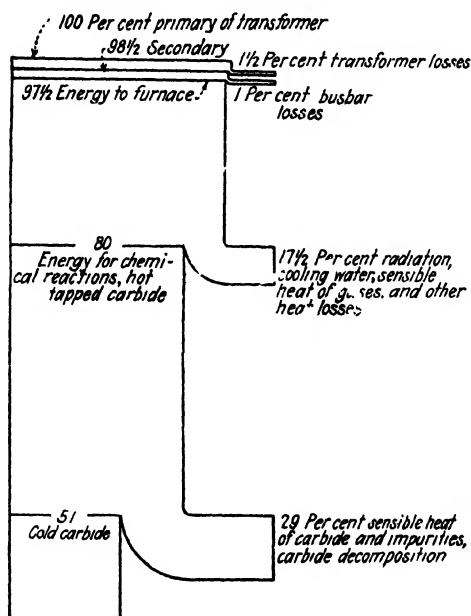
FIG. 226.   Energy distribution in carbide furnace.

A common production is of the order of 8 to 8.5 kg of carbide per kilowatt-day, or about 1.3 to 1.36 kwhr per lb of carbide, with larger furnaces showing lower values.[6]   Covered furnaces

[6] DANNEEL, H., *Z. Elektrochem.*, **36**, 474 (1930), gives a typical energy distribution:

	Expenditure		*the furnace receives*		*the heat of formation*
Kg-cal	2,580,000	→	2,220,000	→	1,370,000
Kwhr	3,000		2,580		1,590
Per cent	100		86		53

	the electric losses	*radiation*	*cooling*		*heat losses through the products*		
					dust	*gases*	*carbide*
Kg-cal	64,500	43,000	258,000	Kg-cal	70,000	72,000	645,000
Kwhr	75	50	300	Kwhr	82	84	750
Per cent	2 5	1 7	10	Per cent	2 7	2.8	25

Consequently, the furnace obtains 86 per cent of the energy, of which 53

or furnaces permitting the recovery of the CO (which is used for burning the limestone to lime) are the more general type.

CALCIUM CYANAMIDE

Calcium cyanamide is produced in electrically heated ovens by the reaction between CaC_2 and nitrogen. The crude cyanamide resulting is a raw material for the manufacture of fertilizers, ammonia, urea, cyanides, insecticides, and fungicides. Some of these are in turn raw materials for synthetic products such as resins, gums, and plastics.

The absorption of nitrogen by carbide was suggested by Frank in 1895, and, with Caro, he succeeded in developing a successful commercial process. The fixation of nitrogen in the cyanamide process is accomplished by bringing practically pure nitrogen gas under slight pressure into contact with finely ground carbide which had been heated to the reacting temperature of 900 to 1100°C. Nitrogen reacts with carbide to form $CaCN_2$ and carbon, according to the reaction

$$CaC_2 + N_2 = CaCN_2 + C + 97,800 \text{ cal}$$

The reversibility of the reaction becomes appreciable above 1360°C with the formation of CaC_2 and the liberation of nitrogen. The nitrification reaction, despite the fact that numerous investigations have been made on it, is not completely understood. It would appear that in an average cyanamide plant 80 to 85 per cent of the carbide charged into the nitrifying furnaces is converted into cyanamide. The balance of the carbide is destroyed, since only a small percentage is found in the cyanamide product. The causes of these losses are not completely known. The presence of oxygen, CO_2, CO, or water vapor in the nitrogen employed will cause decomposition of the carbide and the cyanamide. It would appear, however, that some other factor such as temperature might also be responsible for decomposition losses.

In contradistinction to the carbide reaction, the formation of cyanamide is exothermic. The heat produced by the reaction is utilized to maintain the carbide charge at the reacting temperature. Thus in properly constructed commercial furnaces in

per cent is consumed for the reaction and 30 per cent for the lost heat of the products.

which the reaction is caused to take place, it is only necessary to supply sufficient heat to start the reaction in a portion of the charge.

The rate of absorption of nitrogen by heated CaC_2 is a function of both the temperature and the composition of the charge. In 1894 Moissan[7] found that pure CaC_2 would not react with nitrogen at temperatures below 1200°C. However, Frank and Caro, using commercial carbide, found that nitrogen could be fixed at temperatures considerably below 1200. The nitrogen absorption at temperatures around 1100° was so slow, however, that large amounts of energy had to be supplied to the furnace to maintain the charge at the reacting temperature. From the observations of a number of workers, it was found that alkali and alkaline earth salts such as $CaCl_2$ were catalysts for the reaction. A carbide containing as much as 10 per cent $CaCl_2$ can be made to take up nitrogen equivalent to 18 per cent in 12 to 14 hr at 730°C. Thet heoretical quantity of nitrogen in the final product is 22 per cent. Under the same conditions carbide alone took up less than 1 per cent of nitrogen. Calcium chloride in cyanamide is objectionable since it is hygroscopic and hastens the formation of dicyanodiamide, a decomposition product. The use of $CaCl_2$ has been discontinued. Calcium fluoride shows a catalytic action similar to the chloride. Although the reaction temperature is not lowered as much, it has been found that as little as 2 per cent of the fluoride when intimately mixed with the carbide is sufficient. Calcium fluoride is not objectionable in the final product and appears to be generally used.

A large number of other substances have been found to facilitate nitrogen absorption, among these being CaO, $CaCO_3$, Na_2CO_3, $NaCl$, $LiCl$, $AlCl_3$, K_2CO_3 as examples. Under industrial conditions when large quantities of carbide are used, the heat liberated during the early stages of the nitrogen absorption serves to heat the charge up to 900 to 1100°C, the most satisfactory temperature level for nitrogen absorption. The resulting cyanamide contains 24 to 25 per cent nitrogen.

Furnaces. Two general types of furnaces or ovens are in use, being subdivided into those of a continuous and those of a discontinuous nature. The latter are more common in the United States and will be described first. The ovens consist of an outer

[7] MOISSAN, H., *Compt. rend.*, **118**, 501 (1894).

steel cylindrical shell supported on a reinforced concrete disk. The size having an oven capacity of 1,600 lb of carbide is about 3 ft in diameter and 5 ft in depth; its shell is lined with about 5 in. of infusorial earth or other suitable insulator, and 5 in. of firebrick or refractory. The bottom of the cylinder is covered with insulating brick which is in turn covered with firebrick. The unit is closed by a double cover, the inner one consisting of a hollow iron disk filled with infusorial earth or other thermal

Fig. 227. Cyanamide ovens. (*American Cyanamid Company.*)

insulator and having a 5-in. opening in the center. The outer cover is of sheet steel belled to form a sand seal at the top of the furnace. Typical units are shown in Fig. 227. Nitrogen is fed to the oven through the bottom and also through the side near the bottom. A carbon heating electrode or rod placed in the center of the oven serves to bring the carbide adjacent to it up to the reacting temperature.

The crude carbide used for conversion into cyanamide is broken up and ground to fine powder, of a fineness of at least 85 per cent through a 200-mesh screen.[8] The flow sheet for cyanamide manufacture is given in Fig. 228. The material is pulverized by stage crushing and is ball-mill ground (the final grinding being

[8] "Report on the Fixation and Utilization of Nitrogen," p. 75, U.S. War Department, Washington, D.C., 1922.

Fig. 228. Calcium cyanamide. (*Chemical Engineering.*)

Limestone	4.8 tons	
Coke	1.75 tons	Per ton of nitrogen fixed
Coal	1.0 tons	
Power	9000 kwhr	
Direct labor	16 man hr	
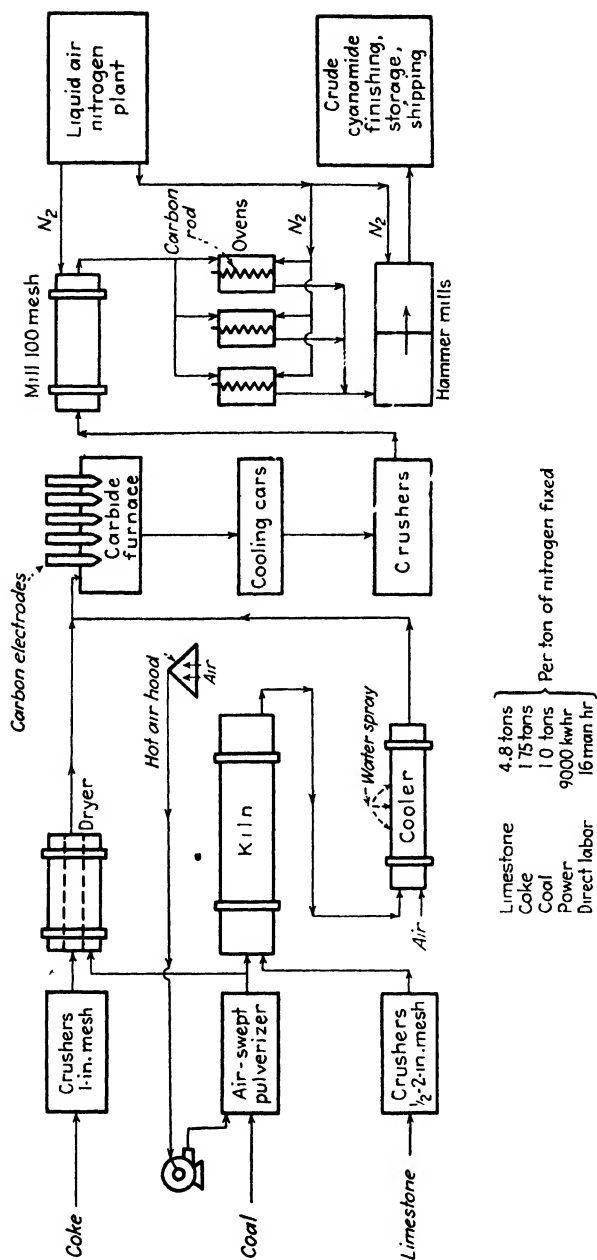
done in a tube mill), at which point catalysts are also added so that they may be intimately mixed with the carbide. Since the material being ground readily reacts with moisture of the air to give acetylene which forms explosive mixtures with oxygen, it is necessary that all the grinding, conveying, and handling of the carbide after it leaves the crushers be done in an atmosphere of nitrogen. Before starting, the air in the mills and conveyors is swept out by dry nitrogen until the oxygen and acetylene percentages do not exceed 2 and 1 per cent, respectively.

The finely ground carbide or carbide charge is placed in a heavy paper cylinder a few inches smaller in diameter than the cyanamide oven. A small paper tube is so placed that it will surround the heating electrode so that the charge is thus held between two concentric cylinders. After the furnace is loaded, the two covers are placed in position, the heating electrode inserted, the nitrogen turned on, and the heating current passed into the oven. The carbide adjacent to the heating pencil soon reaches a temperature of nitrification, and the outer paper cylinder, used as a container for loading the charge, is destroyed after several hours. Heating is continued for a few hours only, until the reaction is well started. The absorption of nitrogen, started at the core of the cylinder of carbide, proceeds gradually outward until the entire charge is converted into cyanamide. The time of nitrification is a function of the composition and physical condition of the charge, the capacity and dimensions of the ovens, etc., but usually varies from 24 to 40 hr. At this time the grayish-black solidly caked mass containing about 24 per cent nitrogen is removed from the oven to cool. A 6-ton ingot of crude cyanamide is shown in Fig. 229. The furnaces at the United States Nitrate Plant No. 2 at Muscle Shoals had a capacity of about 1,600 lb of carbide per charge. It is understood that those at the American Cyanamid plant at Niagara Falls, Canada, are much larger.

The continuous cyanamide ovens have been either of the car or of the tower type. In the former case, in one plant ground carbide was held in sheet-metal·collapsible boxes of about 3-cu ft capacity. About 15 of these boxes were placed on an iron car running on a track through a tunnel oven which was heated and kept filled with nitrogen. Cars were charged at one end of the oven, pushing forward those already in, until, when the oven

was loaded, a car would be discharged at the end for every one added. The nitrogen was introduced at the far end of the tunnel and flowed countercurrent to the travel of the cars. It appears that the carbide boxes were badly deformed by heat and had to be reshaped frequently. Troubles were encountered due to the warping of sections of the oven. A much less uniform cyanamide product was obtained than that produced in other types of ovens. In another design, the carbide in metal boxes

FIG. 229. Ingot of crude cyanamide. (*American Cyanamid Company.*)

moved through a long nitrogen-filled tunnel without the use of cars. The carbide was given a certain amount of agitation, by means of suitable cams, by a combined longitudinal-vertical movement of a section of the floor. The oven was heated electrically by arcs sprung between carbon electrodes extending through the sides of the oven just under the ceiling and a short distance above the carbide. The oven had a capacity of 25 to 40 tons of cyanamide per day.

In the tower type, developed in Sweden, the ovens are cylindrical towerlike structures containing shelves so placed that, when carbide was charged at the top, it was caused to move downward from shelf to shelf by the action of mechanical scrapers or pushers. Nitrogen was fed at the bottom of the oven where the cyanamide was discharged. The heat necessary to start the reaction initially was furnished by carbon arcs near the top of the

furnace.   Temperatures were of the order of 950°C, and about 2 hr were required for the passage of the carbide through the oven. A readily ground lump product containing about 21 per cent nitrogen was obtained.   Mechanical difficulties were encountered in the early development of the furnace.   Caking of the charge during the formation of cyanamide was bothersome.

The efficiency of nitrogen utilization appears to be low for all types of ovens.   In the discontinuous types as generally operated, less than half of the nitrogen entering the oven is actually fixed, although with more careful regulation, it appears that 60 to 75 per cent utilization is possible.   The cost of the nitrogen, however, is a relatively small item, and consequently a low utilization efficiency is not particularly serious.

The composition of the cyanamide produced is a function of the raw materials, the carbide furnace practice, purity of the nitrogen, the operation of the cyanamide ovens, preparation of the carbide, catalysts employed, and the carefulness of operation. The cyanamide ranges from 19 to 22 per cent nitrogen.   The presence of unconverted carbide is objectionable in the processes employed for the conversion of the material into ammonia or for use as a fertilizer.   The material is finely ground and the carbide destroyed by treatment with a spray of water.

CYANIDES

Cyanides are produced from cyanamide by fusion of mixtures of cyanamide, carbide, and common salt in an arc furnace and rapidly chilling the melt.   The reaction is given as

$$CaCN_2 + C + 2NaCl = CaCl_2 + 2NaCN$$

The formation of cyanide is favored by high temperatures and its decomposition by lower ones; hence the cyanide is formed in the arc zone and the fusion product rapidly chilled.   The carbide is added to prevent nitrogen loss during heating.   The furnaces employed have carbon-lined hearths which are relatively wide at the top, tapering down at the bottom.   They are usually single phase equipped with a single vertical electrode, the conducting hearth serving as the other point of current introduction. Current densities are very high so that rapid fusion of the charge takes place.   When the contents of the furnace has reached a temperature of 1300 to 1350°C, it is tapped out into a sump

hole where it is rapidly cooled by mechanical devices. The furnace charge contains 100 parts crude cyanamide to 90 parts of rock salt, and a 90 to 94 per cent conversion of the cyanamide into cyanide is stated to take place, with the production of a grayish-black product containing 36 per cent or better of NaCN. It finds application in the cyanide process for gold extraction and for the production of HCN for fumigation work and the manufacture of insecticides.

CHAPTER 24

NONMETALLIC ELECTROTHERMAL PRODUCTS

Silicon Carbide. Silicon carbide is an important member of the family of synthetic abrasives. In its commercial form it is known as Carborundum, Crystolon, and other proprietary names. In the reduction of silica by carbon at high temperatures a number of different products are produced, among which are silicon monoxide (SiO), metallic silicon, SiC, and an oxycarbide of indefinite composition but approximately Si_2C_2O, termed "amorphous SiC" or "firesand." A petrographic examination of this product shows it to be finely crystalline SiC with varying amounts of unconverted silica and carbon. Greenwood[1] states that an intimate mixture of SiO_2 and carbon at low pressures first evolves CO at 1460°C. A whole series of reversible reactions are possible at temperatures above this, dependent upon the relative proportion of silica and carbon. These are

$$SiO_2 + C \rightleftharpoons SiO + CO$$
$$SiO + C \rightleftharpoons Si + CO$$
$$2SiO + 3C \rightleftharpoons Si_2C_2O + CO$$
$$SiO + 2C \rightleftharpoons SiC + CO$$
$$Si + C \rightleftharpoons SiC$$
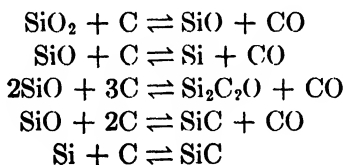
Tone[2] states that silicon melts at 1430°C but is very viscous at this temperature. Exact knowledge of the thermochemistry of the reactions is incomplete. Saunders,[3] from his studies on commercially operating furnaces, gives 1600 ± 50°C as the initial temperature of firesand formation, 1840 ± 30°C as the thermal point of transformation of this product into crystalline SiC, and 2240 ± 5°C as the dissociation temperature of SiC into carbon (graphite) and silicon.

The most important of the reaction products of silica and

[1] GREENWOOD, H. C., *Electrochem. Ind.*, **7**, 119 (1909).

[2] TONE, F. J., *Trans. Am. Electrochem. Soc.*, **7**, 243 (1905).

[3] SAUNDERS, L., *Trans. Am. Electrochem. Soc.*, **21**, 425 (1912).

carbon is SiC. This was given the name of Carborundum by its discoverer Acheson, who in 1891 found the material as a side reaction product in the course of his attempts to dissolve carbon in molten clay for the production of diamonds.

Silicon carbide is prepared commercially in large quantities by heating a suitable charge of carbon and silica sand in a resistance furnace. The carbon is low-sulfur low-ash anthracite, coke, or petroleum coke. Sulfur is avoided because of the SO_2 produced during the operation of the furnace. Iron and aluminum oxides act as catalysts for the dissociation of SiC into graphite and silicon. The silica sand is usually 98 to 99.5 per cent SiO_2. The reactants are mixed in the proportion corresponding roughly to the equation

$$SiO_2 + 3C \rightarrow SiC + 2CO$$
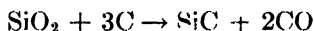
with a slight excess of coke commonly used. Some sawdust may be mixed with the charge to increase its porosity and allow the evolved CO to be more readily released. It was formerly the practice to add some salt to the charge to convert the metallic oxides into volatile chlorides. Several manufacturers use no salt in their product. They purchase the purest raw materials obtainable and find no need for the messy volatilization of chlorides which is harmful in a furnace plant and gives variability in operation. Tone gives the following composition of a ton of fresh charge: sand 0.544 ton, coke 0.351 ton, and if added, sawdust 0.070 ton, salt 0.035 ton. A portion of the mix is usually replaced by unconverted charge from a previous run.

A typical SiC furnace such as is used in making Carborundum brand is shown in Fig. 230 and for the Crystolon brand in Fig. 231. Electrodes are inserted through the heads or ends of the furnace, and a core of granular coke or graphitized material is laid during the loading of the furnace between the ends of the furnace electrodes. When the loading is finished, the charge surrounds the core. The charge is held in place by the side walls of the furnace, which are refractory brick set loosely in place without a bond and supported by iron castings. They are not laid up in fireclay but are retained in steel frames which enclose them firmly. They do not fall out nor are any taken down when the furnace is discharged. Excess of charge on top of the furnace serves as a thermal insulator. During the heating of the charge,
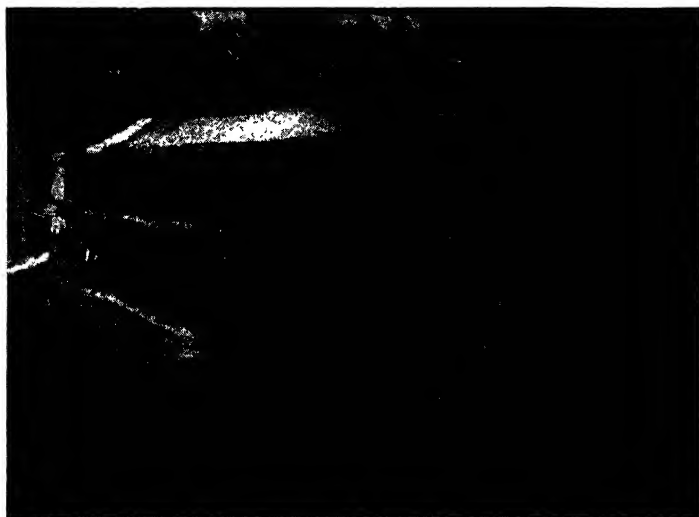
Fɪɢ. 230.   Silicon carbide furnace ready to burn.   (*The Carborundum Company.*)

Fɪɢ. 231.   Another silicon carbide furnace ready for operation.   (*The Norton Company.*)

the CO produced burns at the side and top of the furnace as it works its way out through cracks and minute channels. When the furnace is first put on power its resistance is relatively high, but this decreases as the core heats up. Regulation of the furnace for any given current is thus dependent upon voltage regulation. The efficient working of the furnace is a function of current density on the charge, size of furnace, method of loading, size of core, and rate of heating. The temperature of formation of SiC, 1840 ± 30°C, is relatively close to its temperature of dissociation, 2240°. In normal working, the temperature of the core is about 2350°. Ideal operation would involve a condition in which by far the greater part of the charge reached and was maintained at the temperature of SiC formation, and as little of the charge as possible was allowed to reach a temperature corresponding to carbide dissociation or graphite formation.

Typical furnaces for 2,000-hp size would be 47 ft long, 8 ft high, and 5 ft wide, using an initial voltage between 300 and 200 volts; or 30 ft long, 10 ft high, 10 ft wide operating at an initial voltage of 230.' Energy requirements are from 8,000 to 9,400 kwhr per ton of silicon carbide.

When the furnace is unloaded, the core at the center of the furnace is found to be more or less graphitized. Sometimes there is a ring of graphite immediately adjacent to the core. This in turn is surrounded by the chief product of the reaction, SiC, an iridescent mass of crystals. There is a definite line of demarkation between the graphite and the SiC, and only a very thin layer, if any, containing both materials. The mass of SiC at its outer edges passes imperceptibly into a region of firesand.

[4] The theoretical quantity of energy necessary for SiC production may be approximately calculated from the equation $SiO_2 + 3C = SiC + 2CO - 119,600$ Cal. If the mean temperature at which the SiC is heated be taken as 2100°C and it be assumed that the CO cools down on an average to 1400, and the mean specific heat for SiC between zero and 2100 be taken at 11.3 and that for CO at constant pressure between zero and 1400 about 7.1, the energy required to heat up the SiC is $11.3 \times 2100 = 23,700$ Cal, and for the CO $2 \times 7.1 \times 1400 = 19,900$ Cal. The total heat required will be the summation of these plus the heat of reaction, which will equal 163,200 Cal. The theoretical energy then calculates to 4.7 kwhr per kg or 2.14 kwhr per lb. The energy efficiency of SiC manufacture, where the actual energy is 3.2 to 3.85 depending upon the size of the furnace, calculates to 55 to 70 per cent, the larger furnaces showing the higher efficiencies.

This in turn is surrounded by a shell or layer of unconverted mix, beyond which lie the more readily volatilized materials in the form of a hard crust. If salt has been used in the mix, this shell is largely chlorides distilled from the interior of the furnaces. Crude SiC is removed from the furnace and sent to the crushing plant where the pieces are broken down, subjected to washing, chemical treatment, and magnetic separation. Operating data on silicon carbide production are given in Table 86. The manufacturing flow sheet is given in Fig. 232.

The chemical treatment of SiC consists in boiling it in H_2SO_4, then in a solution of caustic soda, which removes graphite, silicon, and silicides of iron and aluminum. It is then sized by screens and classifiers to give products from 6 mesh down to the finest powders. In this grain form it is ready for use for the

TABLE 86. ELECTRIC-FURNACE ABRASIVES

Operation details	Silicon carbide	Fused alumina
Raw materials... .	Coke, 98 % silica sand, sawdust	Bauxite, coke, scrap Fe
Furnace:		
Type	Resistance	Vertical arc-resistance
Size...	2,000 hp	550 kw
Length	30′	
Cross-section...	10 × 10′	
Cross-section of charge	3′ diameter	
Walls.............	Refractory brick, cast-iron or steel supports	Steel, water cooled
Initial voltage.......	230	100–110
Final voltage................... .	75	
Initial current, amp.....	6,000	2,500
Final current, amp. .. .	20,000	
Current density across furnace charge, amp/sq ft.............	650–2,200	
Core temperature, °C....... . .	2350	
Furnace temperature, °C....... . ·.	1820–2220	2000–2200
Length of run..........	36 hr	
Percentage conversion of material......	70–80	95–100
Energy consumption, kwhr/lb (furnace energy)........................	3.2–3.85	1.0–1.5
Energy efficiency................. ..	55–70	

Sand	1.67 ton	
Coke	1.08 ton	Per ton finished silicon carbide
Sawdust (if used)	0.22 ton	(including unconverted charge)
Salt (if used)	0.11 ton	
Electricity	6400–7000 kwhr	

Fig. 232.   Silicon carbide.   (*Chemical Engineering.*)

polishing of metal or stone, or for further fabrication into grinding wheels, abrasive paper and cloth, sharpening stones, etc. Pure SiC is colorless, but the commercial product is either green, gray, or black and iridescent. This condition is due to a thin film of silica that can be removed by HF with the disappearance of colors. Commercial SiC grains ordinarily contain upward of 98 per cent SiC. Its principal uses are as an abrasive, a refractory, and an electrical heating resistor.

Firesand or amorphous SiC is a by-product of SiC manufacture. It is a grayish-green powder which, like the crystalline material, is very refractory, being useful for furnace linings and crucibles where the furnace atmosphere is of a reducing nature. It is more readily oxidized than is SiC. Its density is 2.7, and when heated to about 1470°C, it is oxidized, giving silica and CO_2. In the absence of oxygen, at a higher temperature, it is converted into SiC.

Silicon monoxide is a gray to brown powder for which uses as pigment, polishing material, and a reducing agent have been suggested but have not found commercial application.

Fused Alumina. Fused alumina was first manufactured by the Norton Company at Niagara Falls under the trade name of Alundum, for use as an abrasive for grinding and drilling and as a refractory. The raw material is bauxite containing a few per cent of oxides other than alumina. These aid in the production of abrasives tougher than when pure alumina is used. The raw material is dried and calcined in advance of fusion. If the analysis of the bauxite be in the correct relation to the desired composition of the product, it constitutes the entire charge; but if other constituents be desired, such as MgO, TiO_2, or Fe_2O_3 not present in sufficient amount in the raw material, they are added to the charge. Various compositions of bauxite are chosen by various users. Almost invariably reducing agents, such as coke, and metallic oxides or metals, such as scrap iron, are added to the charge. These serve the purpose of producing a metal which will settle through the charge with the reduced impurities. The alloy collected from this purification is a somewhat variable grade of ferrosilicon, containing aluminum, titanium, phosphorus, and sulfur, all the latter having been reduced out of the charge. Other fused alumina products are made from previously purified bauxite. The product is gray or white in color.

The furnace used by the Norton Company, shown in Fig. 233, consists essentially of a circular hearth of carbon blocks containing a movable wall fitting into a groove on the circumference of the hearth. This wall is a truncated cone made of sheet steel and may or may not be water-cooled. The furnace is of the arc type. It is placed in operation by striking arcs between the two vertical electrodes and the base of the furnace, single-phase

Fig. 233. Electric furnaces and cooling floor showing large pigs of fused alumina. (*The Norton Company.*)

alternating current being used. As the bauxite fuses, the electrodes are raised, and more charge is fed in, which is in turn melted in the arc between the two electrodes and the electrodes and the base. As the charge builds up, its thickness becomes great enough to prevent arcs between the electrodes and the base, and fusion is caused by the arc between the electrodes. As the bauxite melts, fresh charge is fed in, the electrodes are raised, and the furnace gradually filled. This operation is continued until a block of the fused product is formed. The furnaces are set up in rows, each furnace being on a car. The furnace is allowed to cool, the shell then lifted off the block by a

crane, after which the solidified ingot is picked up by a crane and carried away for cooling. The furnace returns on its track to position for the next charge. Some operating data are given in Table 86.

Tone[5] has described the method of manufacture of Aloxite brand of fused alumina for which the bauxite raw material is first calcined to remove about 30 per cent of water, then mixed with ground coke and iron borings. This mixture is introduced into a circular furnace of the arc type consisting of a steel shell about $7\frac{1}{2}$ ft in diameter and 6 ft high, the bottom lined with carbon. This shell, constituting the sides of the furnace, is water-cooled and requires no lining. The top of the furnace is open. The electrodes are suspended vertically into the furnace. As the mixture is fed in and fused, the ingot is gradually built up. When the furnace is filled, the power is shut off and the ingot allowed to cool and solidify. The product is a crystalline material analyzing about 96 per cent alumina. The impurities have for the most part been reduced and combined with the iron to form silicides of iron and titanium, useful as low-grade ferrosilicon. This alloy settles to the bottom of the furnace and is easily separated. Energy consumption average for the industry ranges from 2,300 to 3,200 kwhr per ton.

The furnaces used by the Carborundum Company are shown in Fig. 234. They are mounted on trucks which travel on tracks so constructed that the furnace shell may be brought under electrodes. After formation of the ingot, the entire furnace may be removed and transported to other portions of the plant, where the ingot is taken out of the furnace and broken up.

When the crude abrasive leaves the furnace room, it is delivered to the crushing plant for conversion into abrasive grains and powders. It is crushed through heavy rolls and then subjected to refining by washing, chemical treatment, and magnetic concentration to remove impurities.

The fused alumina abrasives are not radically different from natural corundum, save in their physical structure. The artificial products show the crystals bound together by a thin matrix of impurities. This condition results in a higher degree of hardness, toughness, and uniformity than shown by the natural product.

[5] Tone, F. J., "Chemistry in Industry," pp. 21–33, The Chemical Foundation, Inc., New York, 1924.

Boron Carbide. Ridgway[6] described the manufacture of boron carbide, B_4C. The manufacturing process is similar to that for SiC, the raw materials being dehydrated commercial boric acid, B_2O_3, and high-purity coke. These are reacted at 2500 to 2600°C in a resistance-type furnace. The innermost zone melts, forming the carbide. Mixed charges or else residues from previous

Fig. 234. Another form of fused alumina furnace. (*The Carborundum Company.*)

furnace runs are piled between electrodes with retaining walls serving as the sides of the furnace. The furnace construction is similar to that employed for SiC, as shown in Fig. 235.

Crystalline B_4C does not distill at high temperatures, inasmuch as it has a very low vapor pressure. The intrinsic hardness of B_4C is greater than that of SiC, being intermediate between this material and the diamond. The material is inert in all solutions of acids and alkalies, both concentrated and dilute. A typical furnace product will have a composition of 97 per cent B_4C, a trace of free graphite, 2 per cent of boron either in the free form or as borides, 0.4 per cent iron, 0.2 per cent aluminum, 0.3 per

[6] RIDGWAY, R. R., *Trans. Electrochem. Soc.*, **66**, 117 (1934).

cent silicon, and 0.1 per cent calcium and magnesium. The most prominent crystalline form is the rhombohedron.

Graphite. The original observation that graphite could be produced in the electric furnace was made as a development of Acheson's earlier discovery of the method of manufacture of SiC. In studying the effect of very high temperatures on SiC, it was found that the material decomposed at 2200 to 2250°C, the silicon being vaporized and carbon being left behind, not in an

Fig. 235. Resistance-type electric furnace used in producing boron carbide. (*The Norton Company.*)

amorphous, but in a graphitic form. Eventually a method was developed for making graphite from anthracite coal.

Graphite is made in an electric resistance furnace such as shown in Fig. 236. The furnace may be considered as a rectangular box built of refractories, through the two ends of which electrodes are introduced. The side walls are formed either of refractory brick laid in place without a bond, or else of concrete blocks. The busbars for the current rise through the floor and are connected directly to the electrode heads, connection being broken at these points when the furnace is off power. Single-phase alternating current is used. Control of the furnace is obtained by regulation of current and voltage or total power input per unit of time. Temperatures of 2200°C or better are reached in the furnace. Furnace operation differs as to whether previously

formed objects such as electrodes or plates are being graphitized, or whether loose graphite or powders are being produced. In the former case the shaped objects are packed in the furnace between the electrodes as closely as possible, and the spaces between them are filled with finely ground carbonaceous material termed "packing dust." Thick layers of this on the top and sides of the furnace serve as thermal insulators.
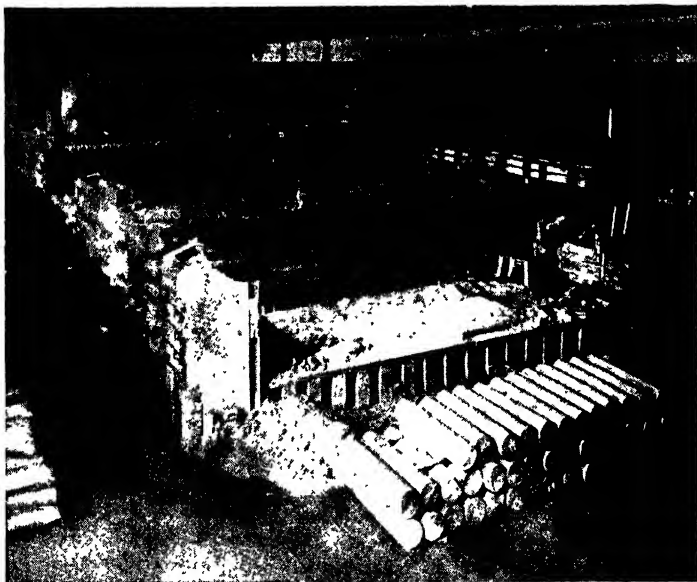
Fig. 236. Graphite furnaces. The furnace in front has been unloaded. The furnace in the rear has been loaded, while of the two in between, one is on power and the other has finished the heating cycle and is cooling. (*International Graphite & Electrode Corporation.*)

The theory of the production of graphite is that carbides are formed by reaction of the amorphous carbon and the metallic and siliceous oxides present as impurities. The furnace, however, soon reaches the temperatures at which these carbides are decomposed, distilling off the metals and metalloids, leaving graphite behind as a result of the decomposition. The packing-material layers serve as a cold blanket in which the metallic and siliceous vapors condense, re-forming carbides to some extent in the layers nearer the center of the furnace and oxidizing them in the cooler

outer portions. It can be seen then that relatively impure material might be used in the manufacture of very pure graphite electrodes, inasmuch as nearly all the contamination is volatilized. The advisability of so doing is questionable, as the volatilization of large amounts of impurities would eventually impart a very high degree of porosity to the electrodes.

In the manufacture of graphite powders the same type of furnace is used, but the raw material is ordinarily anthracite coal, petroleum coke, or sometimes even coal waste or culm. The material is crushed fine and loaded in bulk into the furnace. On the passage of the current, innumerable small arcs are formed between adjacent particles. The mass becomes incandescent and is allowed to remain so until all the impurities have been vaporized, the length of time required depending upon the purity of the raw material.

It is a natural assumption that the higher the carbon content of the charge, the greater will be the amount of graphite obtained. This would be the case provided the carbon were altered directly to graphite. Such alteration, however, does not take place in actual practice. What actually occurs is an indirect alteration consisting in the dissociation of metallic carbides. Fitzgerald,[7] writing in 1904, states that the quantity of graphite obtained is considerably greater and a better product is secured when a coal is used that contains a large amount of foreign mineral substance. There is considerable doubt that, under the present-day practice, the quantity of ash present in the raw materials has the influence on the quantity of graphite obtained, as here stated. No matter what the ash content of the raw material—and all practical raw materials contain some ash—the process is so conducted that the carbon is converted completely into graphite. There is no question of a mixture of graphite and nongraphitic carbon in the finished product; it is all graphite. The amount of ash in the raw material does, however, influence the physical properties of the finished graphite. Acheson's experiments showed that a relatively small amount of the carbide-forming materials can bring about a conversion of a large quantity of carbon into graphite. This amount is much less than that theoretically required. An anthracite coal containing 5.78 per cent ash, which ash is largely silica, alumina, and iron oxide, is

[7] FITZGERALD, F. A. J., "Künstlicher Graphit," W. Knapp, Halle, 1904

converted into practically pure graphite containing only 0.03 per cent ash. Table 87 shows the changes resulting in amorphous

TABLE 87

Amorphous carbons		Graphitized carbons	
Apparent density	Resistivity (ohms per inch cube)	Apparent density	Resistivity (ohms per inch cube)
1 53	0 00172	1 58	0 00056
1 56	0 00158	1 62	0 00057
1 56	0 00161	1 65	0 00051
1 52	0 00170	1 64	0 00047
1 57	0 00162	1 65	0.00042
1.54	0 00146	1 65	0 00046
1 57	0 00151	1 64	0 00035

carbons first baked in gas-fired furnaces and then graphitized. The apparent density is considerably increased, and the resistivity markedly decreased.

Table 88 gives figures for ash, silicon, iron, and copper on certain green electrodes which were first converted into amorphous carbons and later graphitized. The ash content of the green electrode has increased when found in the baked electrode, inasmuch as in baking only the binder is removed and none of the

TABLE 88

Electrode type	Ash, %	Total ash removed, %	Si, %	Total Si removed, %	Fe, %	Total Fe removed, %	Cu, %	Total Cu removed, %
1. Green electrode	9 89		0 20		0 12	..	0 38	
1. Amorphous baked carbon	10 72		0 23		0 19	.	0 33	
1. Graphitized electrode	0 83	92 0	0 03	85 0	0 03	75 0	0 03	92 0
2. Green electrode	7 79		0 06		0 08	.	0 18	
2. Amorphous baked carbon	7 92		0 20		0 17		0 20	
2. Graphitized electrode	0 89	88 3	0 02	66 4	0 02	75 0	0 04	77 5

ash constituent volatilized; but inasmuch as in graphitizing the ash constituents are volatilized, the ash content is shown to be markedly decreased in the graphitized electrode.

The physical properties of the graphites produced, their color,

consistency, luster, hardness, etc., depend upon the raw materials, the rate and length of heating, and manner of cooling. Anthracite coal produces graphites which are variable in character, depending upon the grade of coal used. Some are soft and lustrous, others hard and dull. The specific gravities range from 2.20 to 2.25. For the best quality of lubricating graphites, petroleum coke low in ash content is used. The material is treated with particular care.

The manufacture of graphite electrodes, plates, and other forms is really a branch of the carbon electrode industry,[8] which is discussed under materials of construction. Some operating data in graphite production are given in Table 89.

TABLE 89.   GRAPHITE PRODUCTION

Raw materials	Low-ash anthracite or petroleum coke
Furnace:	
Type.....	Resistance
Size, hp..	1,000
Length, ft.......	30
Cross section of charge . ..	2 ft diameter
Walls............... . .	Refractory brick or concrete blocks
Initial voltage....	200
Final voltage...	80
Maximum current at 200 volts, amp	3,700
Final current, amp....	9,000
C. d. across furnace charge, amp/sq ft. .	900–2,250
Furnace temperature, °C......	2200
Length of run, hr..	24
Percentage conversion of material into graphite..	90–100
Energy consumption, kwhr/lb.....	1.5–1.65
Energy efficiency, % . .	25–30

Fused Quartz. Clear fused quartz is made in the electric furnace from water-clear quartz crystals of the highest quality. The raw material is washed in acids, broken up, and the pieces for treatment carefully selected. There are two distinct steps in the preparation of tubes, rods, ribbons, and sticks. The clean quartz crystals of various sizes are packed as densely as possible into a graphite or carbon crucible, so that, during the cracking of the crystals as the result of heating, the parts cannot separate and

[8] MANTELL, C. L., "Industrial Carbon," 2d ed., D. Van Nostrand Company, Inc., New York, 1946.

allow small amounts of gas to enter the many crevices, giving rise to bubbles. The crucibles are placed in a modified vacuum furnace in which the temperature is raised as quickly as possible to the melting point of the quartz. The pressure in the furnace is maintained at as low a value as possible. The fusion of quartz in vacuum requires 3 to 8 kwhr per lb. The volatilization loss of the material is negligible. The product of this fusion is a clear transparent slug containing comparatively few bubbles. Inasmuch as these were formed at a temperature of around 1800°C, the pressure of the gas inside of them at room temperature is very low. The slug is placed in another graphite crucible suspended in a vertical carbon-tube furnace in which a graphite piston just fitting the crucible presses down on top of the fused quartz slug. A weight is placed on top of a plunger attached to the piston, the slugs are again brought to the melting point, the bubbles are largely collapsed, and by the action of the weight the quartz is extruded in various forms such as rods, tubes, or ribbon. This material is practically free from bubbles, but because of limiting dimensions it may become necessary to rework some of it by the usual blowtorch methods.

Large blocks free from bubbles are made from pure quartz which is fused in a vacuum furnace designed to stand very high pressures. As soon as the material is fused, the vacuum valve is closed, the pressure in the furnace is brought up very rapidly to a sufficiently high point, depending upon the object being made, so that the bubbles are collapsed. It is thus possible to make large quartz blocks freer from bubbles than many kinds of the best optical glass. A typical furnace product is shown in Fig. 237. Furnaces employed are of the resistor type. Because of their relatively large size, they involve many special features of construction.

Fused Silica. Fused silica ware is prepared as the result of the fusion of pure silver sand (99.5 per cent SiO_2) by electric resistance methods, with carbon rod or plate resistors embedded in the sand. The melting point of silica is 1800 to 1900°C, but it must be heated to about 2000° before it is fluid enough to be worked, at which temperature it has a high vapor pressure. Carbon and silica begin to give siloxicon at 1540° and SiC at 1820°, so that there may be complicating side reactions. It would appear that, as the result of the small area of contact

between the carbon and silica, the action is localized and a thin, dense, protective layer of siloxicon or SiC probably forms on the resistors. After enough sand has been melted, the resistor is withdrawn and, by utilizing the hole left in the interior of the melt, the mass is blown out and molded to the desired shape. This is generally done by compressed air, and the articles are fabricated by modified glass-working methods. In the manufacture of tubing, the resistor sometimes consists of a perforated carbon tube. When the fusion is completed, the tube is not taken out but compressed air is forced into its interior and the mass blown into a mold. The crude articles thus fashioned are subsequently trimmed and polished by the use of the oxyhydrogen or oxyilluminating gas flame, the sand blast, and various abrasives. Oxyacetylene gives too hot a flame. Silica shows an appreciable vapor pressure even as low as 1700°C.

Fig. 237. Rough cylinder of pressure quartz 7 in. high as it comes from the furnace. (*General Electric Company.*)

Carbon Bisulfide. Although the major production of CS_2 is the result of the retort process in which the retorts are externally heated, considerable amounts are made electrothermally. The furnace employed is of special construction, of the resistance type shown diagrammatically in Fig. 238. It consists of a circular hearth, through the sides of which four electrodes placed horizontally and symmetrically around the hearth are located. Between the ends of the electrodes are pieces of coke or charcoal, serving as resistors. On top of the hearth is a vertical shaft, through the top of which charcoal is fed. Sulfur enters the hearth through channels in the walls of the hearth and of the shaft. At the operating temperature of the furnace the charcoal reacts with the vaporized sulfur to form CS_2 which passes up

through the shaft and out through a side-arm outlet to condensers in which it is collected. The furnace is fed with two-phase alternating current, the phase currents generally passing between opposite electrodes. It is possible to cause them to pass between adjacent electrodes. Furnace sizes are 240 to 330 kw at 60 volts and 4,000 amp. The energy consumption is 0.4 to 0.5 kwhr per lb. The thermal efficiency of the process is about 42 per cent. Operating details are summarized in Table 92. Control of the furnace is obtained by voltage regulation and rate of feed of the charcoal and the sulfur. To a certain extent the sulfur automatically regulates the furnace, in that, when the hearth becomes too hot, the sulfur in the side-wall feed channels melts rapidly, enters the hearth, rises above the level of the electrodes, and, being a nonconductor, decreases the current. Each

FIG. 238. Carbon bisulfide furnace.

electrode is a bundle 4 ft long and 20 in. square in cross section. They are arranged so that they are 12 in. apart in the middle of the furnace.

Phosphoric Acid. Large quantities of H_3PO_4 are made by electric-furnace smelting of a mixture of phosphate rock, siliceous flux, and carbonaceous reducing agent.[9] The operation is continuous, in that the smelting mixture, properly proportioned according to the analysis of the constituent materials, is continuously fed into the furnace, while the slag and metal (ferrophosphorus formed from the iron in the raw materials) are tapped out periodically. Phosphorus is reduced from the oxides (in complex combination) in the phosphate rock. The phosphorus vapor with the CO produced in the reaction passes up through the interstices of the smelting charge to the top of the furnace, where these gases are burned with oxygen (from air

[9] KLUGH, B. G., Some Considerations in Electrothermal Production of Phosphoric Acid, *Chem. & Met. Eng.*, **36**, 666 (1929).

admitted under controlled conditions) to form P_2O_5 and CO_2. The furnace is totally enclosed. The temperature of the resulting combustion products ranges from 1500 to 1700°C. The gases pass through mains and cooling equipment, after which, at the proper degree of cooling and velocity of gases, the P_2O_5 is hydrated to H_3PO_4 by means of an atomizing water spray. A portion of the concentrated H_3PO_4 thus formed is collected

FIG. 239. Hydrators and precipitators for forming H_3PO_4 and preventing its loss. (*Federal Phosphorus Company.*)

in the hydrating and cooling towers, but the major amount is recovered in Cottrell precipitators. The collected acid is about 85 per cent H_3PO_4, water white, with small amounts of lead, arsenic, and SO_2. The energy requirement is 2.2 to 2.3 kwhr per lb of P_2O_5.

The furnace reactions are given as

$$(CaO)_3P_2O_5 + 5C + 2SiO_2 = P_2 + 5CO + (CaO)_3(SiO_2)_2$$
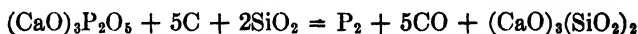
At the present time furnaces are built up to 5,000 kw input, but units twice this size are projected. The precipitators built of carbon blocks are shown in Fig. 239. The furnaces are of the

vertical-arc type with carbon electrodes at the top. A diagrammatic sketch of the furnace which is used for both phosphoric acid and phosphorus is given in Fig. 240. Details of the commercial design of the furnace were given by Curtis and Heaton.[10] Tables 90 and 91 include operating details given by Curtis.[11]

Gases issuing from the electric furnace are essentially 10 parts CO and 1 part phosphorus vapor. The heat of combustion of the gas is divided about equally between the CO and the phos-
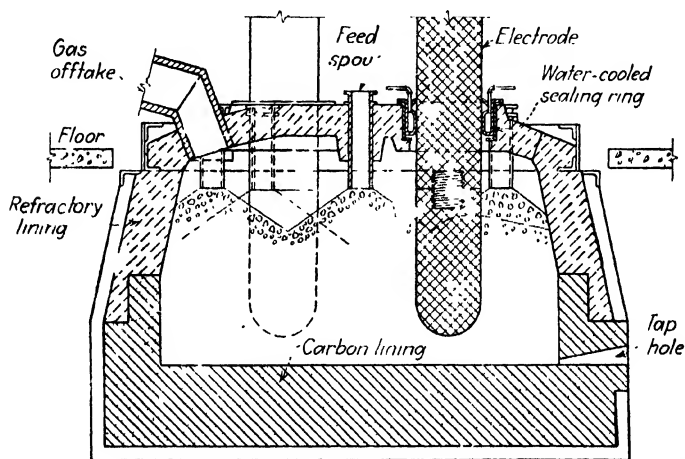
FIG. 240. Schematic cross section of electric phosphate furnace. (*Chemical Engineering.*)

phorus. The dew point of the phosphorus in the gas mixture is approximately 392°F, so that phosphorus may be condensed out and CO recovered. A typical manufacturing flow sheet for the electric-furnace process for phosphoric acid is shown in Fig. 241.

Phosphorus. Phosphorus is produced electrothermally from bone ash, phosphate rock, or crude phosphoric acids with a siliceous slag and a carbonaceous reducing agent. One form of furnace consists of a large gastight refractory-lined iron cylinder containing two large carbon electrodes (entering through the shell), between which the arc passes. Such a furnace is shown in Fig. 242. The charge is heated by radiation. Phosphorus

[10] CURTIS, H. A., and HEATON, R. C., *Chem. & Met. Eng.*, **45**, 536 (1938).
[11] CURTIS, H. A., *Chem. & Met. Eng.*, **42**, 320 (1935).

Phosphate rock (35 6 P₂O₅) 3970 lb   Iron (depends on ferrophosphorus requirements)⎫ Per ton
Silica rock   1270 lb   Electricity   3460 kwhr ⎬ 85%
Coke   748 lb   Direct labor   (est) 05·l man hr ⎭ H₃PO₄
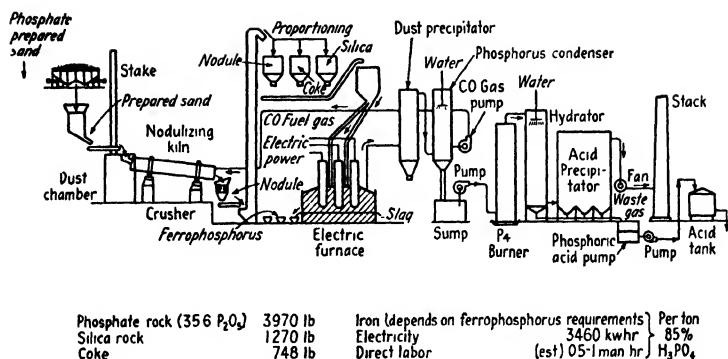
FIG. 241. Phosphoric acid (electric-furnace process). (*Chemical Engineering.*)

TABLE 90. MANUFACTURE OF PHOSPHORIC ACID

Raw material	Phosphate rock, silica, coke	
Furnace:		
Shape....................	Rectangular	Cylindrical
Dimensions, inside....	9 ft. 8 in. × 19 ft. 3 in.	15 ft. 4 in. max. diam.
Maximum depth	8 ft.	
Lining..........	Carbon blocks	Carbon blocks
Size..................... .	6,000 kw.	6,000 kw.
Capacity, tons P per day.. ...	10	
Electrodes:		
Number......	3	3
Size.............	30 in. diam.	30 in. diam.
Spacing......... ..	5 ft. 9 in.	Corners of triangle 5 ft. 9 in. sides
Feed........	Continuous	Continuous
C.d. per square inch cross section..	26–27	26–27
Method of feeding furnace	Hoppers around electrodes	Hoppers around electrodes
Exit temperature of gases, degrees Fahrenheit....................	450	
Slag tapping....................	Continuous	Continuous
Power consumption:		
Kilowatt-hours per ton P₂O₅...	4,800	
Kilowatt-hours per pound P₂O₅..	2.2–2.3	
Pounds P₂O₅ per kilowatt-hour.	0.43–0.45	

TABLE 91. COMPOSITION OF RAW MATERIALS IN PHOSPHORIC ACID
MANUFACTURE

Constituent	Brown rock, per cent	White rock, per cent	Silica, per cent
P_2O_5.	33.1	31 3	
CaO...	44.6	45.4	
SiO_2....	5.0	10.2	95.0
Fe_2O_3........... ..	3.3	1.8	
Al_2O_3....	3.4	1.8	
CO_2.............	1.1	2.0	
F....	3.4	3.3	
Moisture	1 5	0.1	

Coke, per cent

Volatile matter.... .	1 9
Fixed carbon	84.3
Ash... .	13 8

Charge, pounds

Brown rock	2,000
Silica...	718
Coke ..	324

TABLE 92. VOLATILE PRODUCTS OF THE ELECTRIC FURNACE

Operation details	Phosphorus	CS_2
Raw materials	Bone ash or phosphate rock, coal, and SiO_2	Charcoal, sulfur
Furnace:		
Type..	Arc, carbon lining, vertical electrode	Resistance, 2-phase a c., shaft feed
Capacity, kw	10,000	240–330
Current, amp.		4,000–6,000
Voltage.. . .		60–150
Temperature, °C .	1150–1450	
Production per 24 hr, lb		14,000
Energy consumption, kwhr/lb	4.0–5.5	0.4–0.5
Thermal efficiency, %.		30–45
Percentage P recovered.	80–90	

distills off and is collected under water in condensing equipment. The slags are drawn off intermittently. Charging of the furnace is a continuous operation. Phosphorus recovery is usually of the order of 80 to 90 per cent, more favorable results being obtained with low iron content of the charge. Reaction between the bone ash or phosphate rock and the carbon begins at 1150° and is complete at 1450°C. Present-day furnaces are 10,000 kw in size. Operating details are summarized in Table 92. The raw materials are the same as for phosphoric acid, and the furnaces are of the same type. The phosphorus is condensed, stored, and shipped in tank cars under water. From the economic viewpoint shipment as elemental phosphorus is more economical than transportation in the form of H_3PO_4 or phosphates.

Fig. 242. Vertical section of phosphorus furnace.

Part V

ELECTROCHEMISTRY OF GASES

CHAPTER 25

ELECTRICAL DISCHARGES IN GASES

The electrochemistry of gases is complicated by difficulties which do not arise in electrolysis. Although it is questionable that this phase of the subject will ever be as fruitful as the electrochemistry of liquids, there have been many developments of considerable importance in recent years, particularly in relation to gaseous reactions which take place under the influence of ionization.

Ionization of Gases. In the normal state gases are among the best insulators of electricity. In air at ordinary pressure a potential difference of several thousand volts is required to produce a spark 1 cm in length. Gases may be rendered partially conducting by the action of agents such as cathode rays, the α, β, and γ radiation emitted by radioactive substances, certain chemical reactions, high temperatures, and the action of the photoelectric effect of short wave-length radiation. Factors such as these are termed "ionizing agents."

The conductance of electricity by gases is assumed to be due to the breaking up of the gas into positively and negatively charged particles which, by analogy to the carriers of electricity in electrolytic conductance, are called "gaseous ions." In accordance with the electron theory of the structure of matter, gaseous ions consist of atoms or molecules which have gained or lost one or more electrons, or of electrons themselves.

Electrical Discharges through Gases. The character of an electrical discharge through a gas varies markedly with the gas pressure. With decreases in pressure the spark broadens out with the assumption of a brushlike appearance and a bluish color. At pressures as low as 0.5 mm the gas becomes luminous, showing a series of transverse flickering bands or lines. Rays can be observed moving in straight lines from the cathode if the pressure be very low. These have been termed "cathode rays" and were shown by J. J. Thomson to consist of electrons,

659

each with a mass of 9.0×10^{-28} g and a charge of 4.7×10^{-10} electrostatic unit. The electron is regarded as an atom of electricity.

If a potential difference exist between two parallel plates set in a gas which is influenced by an ionizing agent, a flow of electric current between the plates will result. The negative ions, under the influence of the electric field between the plates, will move to the positive plate and the positive ions to the negative plate. With a weak electric field the mutual attraction of the ions will cause a number of them to recombine before reaching the plate. The resulting current is then small. The stronger the field the greater will be the current strength until the so-called "saturation current" is reached, when all the ions formed arrive at the plates.

Inasmuch as cosmic rays cause some ionization of molecules of matter, any space containing matter shows electrical conductivity when considered in the absolute and not in the relative sense. This conductivity may be determined by mechanisms sensitive enough to measure the current flowing between two conducting surfaces and its relation to the applied voltage.

Very small currents may be caused to pass through the gas between electrodes. If the voltage between electrodes be raised, the potential gradient along the path which the ions take will become steeper, and the velocity of the ions will increase. Collisions between ions and neutral molecules are constantly occurring. With a sufficiently high potential gradient we may obtain ionization by impact with increased conductivity of the gas. Probably the earliest chemical reaction effects due to electrical discharges were observed in connection with the odors of ozone and oxides of nitrogen formed by flashes of lightning which caused intense ionization.

The self-sustained electrical discharge readily lends itself to ionization studies as well as to the effect on chemical reactions with attendant phenomena of light production. The glow discharge, the silent electrical discharge, and the electrodeless discharge or corona will be discussed. Arc phenomena with particular reference to electric furnaces have been discussed earlier in this volume.

Consider a glass tube as in Fig. 243 with neon at a pressure of 5 mm of mercury. When 100 volts or so are applied to the tube,

a very small current will flow.   Natural ionization of the gas produces sufficient conductance.   When the voltage is increased, a point is reached when the tube becomes luminous and a relatively large current will flow.   Such a device is the basis of the widely used neon signs for lighting and advertising display. The luminosity is not uniform under certain conditions and dark regions exist.   The glow discharge has been divided in accordance with Fig. 243.   At the cathode, electrons are liberated, probably
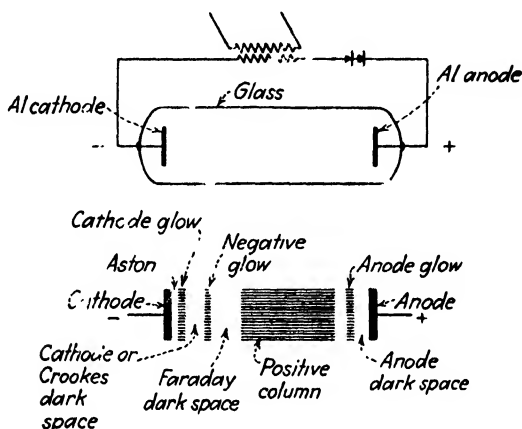
FIG. 243.   Self-sustained glow or luminous discharge.

to the greatest extent by bombardment of positively charged ions.   As the electrons pass through the field around the cathode, they gain kinetic energy and can impact molecules and set free more positive ions, which in turn liberate more electrons when they discharge at the cathode.   The Aston gas space is located where the electrons leaving the cathode gather speed and then excite the gas to luminosity, resulting in the cathode glow.

Most of the excitations which have been studied reach a peak as a function of certain electron velocities; increased speeds cause less excitation and less radiation, as shown by the Crookes or cathode dark space.   But the electrons have reached velocity and energy levels so that they may ionize the gas and cause secondary electrons, which in turn gather enough energy to excite other molecules and cause another luminous band, the negative glow.   In this section the potential or voltage is, for

all practical purposes, constant, but a large drop in potential takes place in the preceding Crookes dark space.   This potential drop is that of the metal-gas electrode system and varies with the distance from the cathode.   Beyond the negative glow, the electrons no longer are able to resonate, and the Faraday dark space appears.   This will extend almost to the anode if there are no confining walls.   The electrons must acquire sufficient speed to reach the anode and are thus able to cause luminescence in the form of the anode glow.   With enclosing walls the electrons attain velocities high enough to cause excitation and ionization which results in the positive column luminous area.

Electron impacts as ionizing forces introduce a number of possibilities in causing compound molecules to break up and to force simple molecules and ions to enter new combinations. The possibilities must be different in the various sections of the glow discharge.   Electrons and molecules may simply bounce off each other and suffer only change of direction.   Fast-moving electrons may hit molecules hard enough to form positive ions and slow-moving electrons, and the positive ions may cluster with molecules.   In other cases fast-moving electrons may by impact raise neutral molecules to an excited state, the higher energy level being in turn reduced by radiation.

Brewer and Westhaver[1] showed that the negative glow was the seat of greatest chemical action in ammonia synthesis and that compound formation occurred only in the luminous discharge areas as indicated in Fig. 244.

Application of glow phenomena has resulted in the commercial development of gaseous conduction lamps, based on the principles discussed above and well known in the form of the Geissler tube of the physicist.   Moore[2] developed high-voltage nitrogen- and CO_2-filled lamps.   The low-voltage low-wattage neon lamp was an outgrowth of this work.

The lamps are all glow tubes; but commonly, to obtain electron emergence readily, the cathodes are heated to emission temperature by circuits which are adjuncts to those essentially of the discharge circuit.   The colors produced are a function of the spectral emission of the excited gases in the tubes: red from pure neon, greenish blue from mercury, blue from mercury and neon

[1] BREWER, A. K., and WESTHAVER, J. W., *J. Phys. Chem.*, **34**, 153 (1930).
[2] MOORE, D. M., *Trans. Illum. Eng. Soc.*, **15**, 209 (1910).

combinations; as well as modifications produced by the color of the tube itself: yellow from sodium, etc.

Sodium lamps contain no vapor, as the sodium is solid when cold. Neon is commonly used as a filler at 2 to 5 mm of mercury. Auxiliary heating vaporizes the sodium, which vapor serves as the gaseous conductor. Buttolph[3] outlined electrode design and operation and the effects of glass, bulbs, vapors, and other factors in gaseous conduction lamps. Werfhorst[4] stated that in sodium-
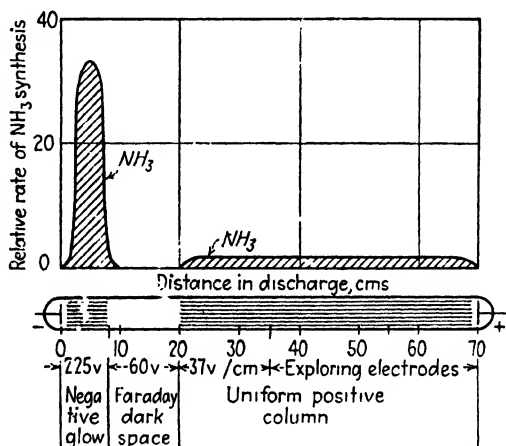
FIG. 244. Seat of ammonia synthesis in glow discharge.

vapor lamps borosilicate glass was necessary to withstand the corrosive action of sodium. Automatic ignition is accomplished by the use of small amounts of neon and a heated cathode of the oxide-coated type.

Cotton[5] described the crossed discharge, which has a glow. The glow does not fill or pervade the reactor tube as does the usual glow discharge, but it has definite boundaries to its luminous volume. This glow is most pronounced in air at 335 mm Hg as compared with maximum pressures of 10 mm for the usual glow discharge.

The temperature of the exit gas is only slightly greater than the temperature of the entering gases and, under certain con-

[3] BUTTOLPH, L. J., *Trans. Electrochem. Soc.*, **65**, 143 (1934).

[4] WERFHORST, G. B., *Trans. Electrochem. Soc.*, **65**, 157 (1934).

[5] COTTON, W. J., *Trans. Electrochem. Soc.*, **91**, 407–417, 419–436 (1947).

ditions, may even be at a lower temperature. Metallic lithium electrodes, which melt at 186°C, can be used and show no signs of softening even at the sharpest edges. Hydrocarbon gases, such as methane, benzene, or gasoline, mixed with air passed through the discharge show little or no tendency to explode.

This type of discharge shows a low energy density, *i.e.*, total watts supplied to the discharge divided by the volume in cubic centimeters of the luminous discharge.

Crossed discharges result in unexpectedly high activation of gases and relatively high yields of reaction products.

Research workers have sensed the possibility of catalyzing chemical reactions in an electric field of certain critical frequencies. Cotton showed that such critical frequencies exist and that, as a result of applying such critical frequencies, the speed of reaction is greatly increased and the chemical and the energy yields are also greatly increased. Frequencies that catalyze a given reaction appear to be dependent solely upon the nature of the reaction and independent of the electrode materials used. Critical reaction frequencies of a given series are related one to another.

Silent Electrical Discharge. In contrast to the luminous discharge, other forms operate at higher pressures. These forms include the point discharge, the silent electrical discharges as produced in ozonizers, and the corona. In the point-plate type of discharge, when the points are negative and serve as cathodes, the usual cathode dark space and negative glow are developed. At ordinary pressures these are so small in magnitude that they are visible only when magnified. Glockler and Lind[6] reviewed ozone production by this discharge, and Moeller[7] and Rideal[8] outlined the theoretical and practical aspects of the subject.

Ozone. Ozone is formed from oxygen according to the reaction $3O_2 \rightarrow 2O_3 - 68,200$ Cal. At ordinary temperatures it is a strong-smelling gas with powerful oxidizing and bactericidal properties. It finds application in water purification, deodorizing, refreshing of air, and oxidizing and bleaching. The con-

[6] GLOCKLER, G., and LIND, S. C., "The Electrochemistry of Gases and Other Dielectrics," John Wiley & Sons, Inc., New York, 1939.

[7] MOELLER, M., "Das Ozon," F. Vieweg und Sohn, Brunswick, 1921.

[8] RIDEAL, R. I., "Ozone," D. Van Nostrand Company, Inc., New York, 1920.

centrations used are 0.01 ppm for ventilation, 0.05 ppm in the destruction of moderate odors, 0.1 ppm in the removal of pronounced odors, 0.5 ppm for the prevention of bacterial and fungi growths, and 10.0 ppm for disinfecting and deodorizing over a very short period of time. The proportion of ozone in the equilibrium mixture with oxygen is very low, but increases as the temperature rises. At 1300°C it is 0.1 per cent, at 2000° 1 per cent, at 4500° about 10 per cent. It is possible to produce ozone by heating oxygen to a very high temperature and suddenly cooling it. Rapid decomposition causes low concentrations. Ozone is produced photochemically by ultraviolet light of 120 to 180 mμ, but commercial sources of ultraviolet light do not afford efficient ozone production, since light of greater wave length (300 to 330 mμ) exerts a decomposing effect on ozone and ultraviolet lamps are richer in these longer waves than they are in the shorter.

The use of the silent electric discharge at room temperature allows the production of ozone until a definite electrical equilibrium has been reached which corresponds to a thermal equilibrium at a higher temperature. Thus appreciable ozone concentration may be produced.

Ozonizer designs avoid conditions which will produce more than one type of electric discharge. Edge discharges are very critical of voltage and should be avoided in high-concentration ozonizers. In the production of ozone by the silent discharge, an equilibrium is reached dependent upon conditions such as pressure; temperature; moisture content of the air or oxygen; shape, size, distance apart, finish, and age of the electrodes; types of current, whether alternating current or direct current and, if alternating current, its frequency and wave form.

As the degree of ionization in an ozone generator is intense, dust and vapor present in the air passed through will become charged and deposited on the electrodes. Myriad minute points, from which sparking discharges take place, will form. These in turn produce oxides of nitrogen that become absorbed by the deposited water and are ultimately oxidized to HNO_3, which in turn attacks the metallic parts of the generator. The presence of both sparking discharges and oxides of nitrogen reduces the ozone yield.

An ozone generator is an energy converter. It converts

electric into chemical energy. Its output in chemical energy is a function of its input in electrical energy, together with the rate at which air is supplied to the discharge. This latter consideration becomes essential through the existence of "limiting yields" which are progressively displaced directly as the air flow, up to the point of equilibrium.

With increasing air flow the concentration decreases with increasing yields. This is illustrated by the curves in Fig. 245. Beyond the 30-liter ordinate, the extra cost of drying the addi-
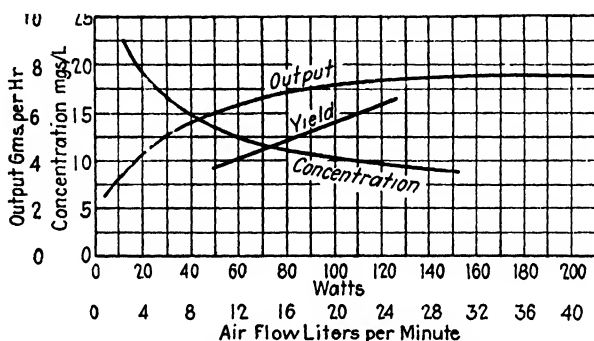
FIG. 245. Air-flow output, air-flow concentration, energy-input yield curves.

tional air so offsets the value of the increase in yield as to make it uneconomical to attempt to realize the full value of the curve.

Commercial Forms of Ozonizers. Commercial ozonizers are equipped with air filters and dehydrators for purification of the air. In large units moisture may be removed by refrigeration. Commercial designs of ozonizers differ in details such as the number, nature, and arrangement of the dielectric plates; type of cooling; the shape, size, and location of electrodes; as well as external electrical equipment. They may be divided into three classes: the discharge taking place through the path (1) metal-dielectric-air gap-metal; (2) metal-dielectric-air gap-dielectric-metal; and (3) metal-air gap-dielectric-air gap-metal.

The Siemens and Halske ozonizer consists of an iron box provided with glass windows. A number of vertical glass cylinders coated on the outside with metal pass upward through the bottom of the box. They serve as one set of electrodes, the others being cylinders of sheet aluminum set concentrically

inside these boxes. Water is run through the iron box to cool the apparatus. The voltages applied range from 7,000 to 12,000. Production is at the rate of 50 g of ozone per kilowatthour at a concentration of 2.5 g per m³ when 500-cycle current is used. The yields are considerably lower when 60-cycle transformers are employed. The Vosmaer ozonizer is of the grid type in which the grid, both frame and crosspieces, consist of a single metal casting. Both sides of the crosspieces are covered with a glass dielectric. Electrodes are suspended in the middle of the different sectors, being insulated from the frame. They present knife-edges to the dielectric surfaces. Applied voltages are about 10,000 at a production of 50 g of ozone per kilowatthour and a concentration of 1 g per m.³ The unit sizes are 100 to 1,000 watts.

The Abraham-Marmier has plane-surface electrodes with a layer of glass dielectric on either side. The electrodes are arranged in a parallel row inside a box. For water cooling, the electrodes are made in the form of metal boxes through which the water passes. To avoid short-circuiting, the flow is not continuous but is interrupted. Air is introduced by a tube passing through the metal of the ozonizer and the electrode system, being provided with holes at points corresponding with the air gaps between the plates.

The United States Ozone Company ozonizer has a cylindrical glass dielectric designed so that edge discharges are eliminated, with an aluminum cylinder enclosing the dielectric and forming an annular space with it. The units are operated at an energy density of 0.5 watt per sq in. of active electrode surface. The aluminum cylinder has cast endpieces carrying inlet and outlet ports. It acts as one electrode. The other consists of a metallic sheet deposited upon the walls of the dielectric tube. The units are mounted vertically.

From the heat of reaction, the theoretical energy for the production of 1 gram mol of ozone from oxygen corresponds to a theoretical formation of 1,200 g ozone per kilowatthour. Even when operated at low concentrations, commercial ozonizers show energy efficiencies of the order of 5 to 15 per cent.

Corona Discharge. The corona or crown discharge observed near highly charged wires or high-voltage lines is another manifestation of the same cause as the discharge near a point. The

electric field is high near the electrode of high curvature (as a point or projection or rough section). Ionization results, and a self-sustaining discharge with luminous sections is established. The chemical reactions obtained should be of the same nature as the point discharge. The corona discharge is of importance in "electrostatic precipitation."

Electrostatic Precipitation. The "precipitation" or removal of suspended particles from gases by electrical means is accomplished through the use of a strong electric or so-called "static" field. An electrically charged particle when in an electric field between two electrodes tends to move toward the negative electrode if the charge be positive and toward the positive electrode if negative. The suspended particles receive electric charges in two ways: (1) if the particles be suspended in gases which are "ionized," they receive charges from the gases directly; (2) if the gases pass through an electric field, they receive charges by "induction."

A strong electric field will cause ionization of a gas. The familiar corona discharge is evidence that this ionization is taking place. The gas molecules or what remains of them are charged positively and are called "positive ions"; the negative electrons may remain free, or they may become attached to neutral molecules and so make up negative ions. The ions and electrons become attached to the suspended particles. The resulting agglomerates move across the electric field because of the force exerted by the field upon the unbalanced electric charges they carry. It is probable, however, that precipitation is more largely due to ionization of the gases than to induction.

If, in apparatus for the electrical precipitation of suspended particles, one of the electrodes be filamentary or have sharp points or edges, and the other electrode have a smooth and extending surface, it is possible by impressing a high voltage across the electrodes to obtain ionization of the gases and to cause any liquid or solid particles suspended therein to be precipitated upon the electrode with the smooth surface. An example of such apparatus is a smooth pipe having a fine wire held axially in but insulated from the pipe. The pipe is connected electrically to ground and the wire is connected to a source of high-tension current. The gases to be treated pass through the pipe, and as they pass between the discharge and collecting electrodes,

they act as part of the electric circuit, the ions made in the gases acting as carriers of electricity from one electrode to the other.

For electrical precipitation work, direct current is found to give much better results than alternating current. The best results are obtained when the ionizing or so-called "discharge electrode" is of negative polarity. By making the electric field around the ionizing electrode very intense, it is possible to keep particles from being deposited upon it; practically all the suspended material is deposited upon the smooth or collecting electrode which has an extended surface, the electric field adjacent to such surface being relatively weak.

This characteristic of the particles to migrate toward the weakest part of the field may be explained in part by the phenomenon commonly called "electric wind." The molecules of the gases which have become ionized and the suspended particles to which electric charges are attached are propelled rapidly through the gases by the force of the electric field. The movement of these particles and molecules has an aspirating effect upon adjacent gas molecules, setting them in motion, the direction being from the strongest to the weakest part of the field. Charges of both positive and negative sign are present in the gases. They tend to move in opposite directions, but those which tend to move countercurrent to the electric wind have to overcome considerable resistance and are probably swept back or neutralized, especially if these charges are endeavoring to take suspended particles with them. By making the central electrode of negative polarity, the movement of the gases is set up by electrons and negative ions which have a higher velocity than positive ions. The results described above are then the most pronounced and satisfactory.

In practice, a precipitator consists of a multiplicity of opposed electrode units, one group formed in such a manner as to facilitate corona discharge, the other being of a type to minimize or prevent discharge therefrom. The former are usually referred to as "discharge electrodes," the latter as "collecting electrodes." Discharge electrodes may consist of wires, chains, edged strips, serrated edges, or any form of conductor that will establish a sufficiently high potential gradient at or near its surface to cause corona discharge. Collecting electrodes may be pipes,

plates, screens, closely grouped wires, or any other form or arrangement of conductors that will establish low field concentration and thus minimize or prevent corona discharge.

The collecting-electrode system is ordinarily of much greater weight than the discharge system and is therefore electrically grounded. The discharge-electrode system is mounted upon insulators, being usually negatively charged with respect to ground. The potential difference maintained between electrodes is dependent upon their spacing, among other factors. In different installations it ranges from 20,000 to 100,000 volts. Unidirectional current is supplied by rectifying high-tension alternating current. The precipitator has been given the name of "treater," the type being designated by the form of collecting electrode used, as for example, pipe treater, plate treater, graded-resistance treater, etc. The principle of precipitation is the same in each case, the choice of treater depending upon circumstances dictated by engineering considerations.

As the voltage is raised above the critical potential, a corona discharge is established. The gas adjacent to the discharge electrodes is ionized, and the resultant ions travel in the direction of either the collecting or the discharge electrode, depending on whether they be negative or positive. Those ions which leave the zone of ionization, however, travel to the collecting electrode where they give up their charge. Any suspended liquid or solid particles carried by the gas that passes between the electrodes will acquire a charge and be forced out of the gases to the electrodes.

In practice a certain amount of precipitated material is always collected upon the discharge electrodes, but the ground collecting electrodes receive by far the greater portion of the precipitate. Liquid material brought to the electrode will flow off continuously. If the precipitated particles be solid, however, they are allowed to collect for a certain period, then are mechanically shaken off by knocking into hoppers placed beneath the electrode system. These hoppers are then sent on to the point of utilization or disposal.

The precipitator has found wide application in the metallurgical, cement, and chemical industries and in connection with blast furnaces in central power stations. The pioneer work and its reduction to engineering practice as regards equipment and

construction were done by Cottrell,[9] and electrostatic precipitators are commonly known as Cottrell precipitators.

The phenomena of the glow discharge have been discussed. If the current-voltage relations be plotted for a pair of electrodes in a point-plate system, curves similar to Fig. 246 where the point is positive, and Fig. 247 where it is negative, will be obtained. Current increases after the glow discharge has been established will cause discontinuity, and the sparking variety of brush dis-
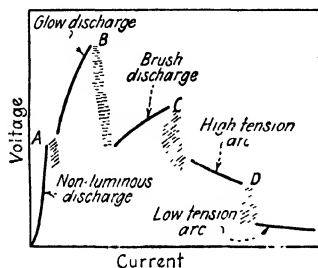
FIG. 246.
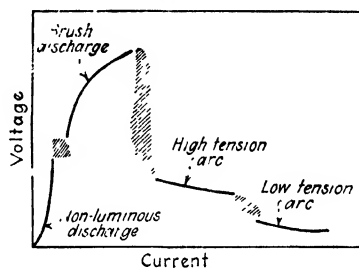
FIG. 247.

charge will take place at lowered voltage. Ionization of the gases between the electrodes has become greater and the potential between the electrodes less, as the intervening space is a better conductor. Increasing the voltage now again causes current rises to a point of discontinuity when the high-voltage arc, with volatilization of the electrodes, sets in. Here the electrical characteristic is negative; *i.e.*, increasing currents are possible with lowered voltage. A further break occurs, and the stable low-voltage arc is established, of a variety common in electric furnaces.

With point electrodes, as between pencils of carbon (omitting the crater effect), curves similar to Fig. 247 are obtained.

Mobility of Gaseous Ions. The velocity of a gaseous ion is a function of the strength of the electric field acting on it. For a specific gas under definite conditions of temperature and pressure, the velocities or mobilities, u and y, of the positive and negative ions, respectively, are

$$u = k_1 x$$
$$y = k_2 x$$

[9] COTTRELL, F. G., *J. Ind. Eng. Chem.*, **3**, 542 (1911); *Smithsonian Inst. Pub., Ann. Rept.*, p. 653, 1913.

where x is the strength of the field and k_1 and k_2 are constants. The constant k is equal to one-half the product of the charge on the ion and the time required for the ion to describe its mean free path, divided by the mass of the ion. Table 93 gives the values of relative mobilities of gaseous ions at ordinary temperatures and pressures.

TABLE 93. RELATIVE MOBILITIES OF GASEOUS IONS

Gas	k_1 (+)	k_2 (−)
Hydrogen...............	6.70	7.95
Air..............	1.36	1.87
Carbon monoxide..	1.10	1.14
Carbon dioxide.......	0.81	0.85
Sulphur dioxide....	0.44	0.41
Pentane........................	0.35	0.35

The relative mobilities of the ions vary inversely as their molecular weights. In the lighter gases the negative ion has a higher mobility than the positive ion. The difference decreases in inverse proportion to the molecular weight, so that in the gases of higher molecular weight the ionic mobilities of the positive and negative ions are the same. The value of the constant k depends, among other factors, upon the time required by the ion to describe its mean free path, which in turn is in inverse proportion to the pressure of the gas. It follows that the product kp, if the nature of the ion does not change, will be independent of the pressure. With positive ions the value of this product does not change with decrease in pressure, thus indicating that this ion consists of a single charged atom or molecule. In the case of negative ions the value of kp increases rapidly as the pressure of the gas is decreased below 0.1 atm. The negative ion thus becomes smaller as the pressure of the gas is reduced. At low pressures the carriers of negative electricity are smaller than an atom or molecule. It follows that negative ions, formed by the union of electrons with neutral atoms or molecules, lose electrons at low pressures.

Ionizing Potentials. A current passing through partially ionized gas, above its saturation value, will increase as a result of increased ionization, which in turn is caused by collisions between electrons and neutral gaseous molecules. The velocity and

energy of the electrons will vary directly with the strength of the electric field. With velocities of the order of 10^8 cm per sec, a moving electron on colliding with a neutral molecule will completely remove an outer electron, leaving the molecule positively charged. To accomplish this removal, the active electron passes through a potential drop termed the "ionizing potential" of the gas. It represents the work necessary to remove an electron from a molecule. The ionizing potential is not a perfectly definite quantity, because of its dependence upon the manner in which the work is done.[10] A gas may have several such potentials, representing the removal of varying numbers of outer electrons.

If the electron velocity be not sufficiently high to remove an electron entirely from a molecule of gas, the impact may at least displace one. This also involves a fall of potential, the minimum value of which is called he "resonance potential" of the gas. Each kind of atom will, of course, ha e many resonance potentials.

A result of the displacement or removal of an electron from a gaseous molecule or atom is the appearance of spectral lines having definite wave lengths. From these the ionizing and resonance potentials E of a gas may be determined, using the equation

$$E = \frac{hc}{e\lambda \times 10^8}$$

where c is the velocity of light, λ is the wave length of the spectral line, and h is the quantum constant (7×10^{-27} erg per sec). The simple ionizing potentials of some of the gases are given in Table 94.

Thermionic Emission. If the temperature of a hot body be sufficiently high, the body will not hold an electric charge but will give off positive and negative ions, which, although really electrons or positively charged atoms, are termed "thermions." The electric current from such a body is called a "thermionic current." The temperature required for its production is a function of the type of body as well as the nature and pressure of the surrounding gas. For example, platinum in vacuum requires a temperature of about 1000°C to give an appreciable thermionic current, whereas a noticeable effect is produced at 300° with

[10] THOMSON, J. J., "The Electron in Chemistry," p. 21, Franklin Institute, Philadelphia, 1923.

TABLE 94. IONIZING POTENTIALS OF GASES[1]

Gas	Ionizing potential, volts	Gas ·	Ionizing potential, volts
Caesium...............	3.877	Zinc..................	9.353
Rubidium..............	4.158	Iodine........	10.1
Potassium.............	4.321	Mercury.	10.392
Sodium................	5.116	Arsenic.....	11.5
Lithium...............	5.368	Sulphur..............	12.2
Barium................	5.188	Hydrogen.............	13.3
Strontium.............	5.670	Phosphorus......	13.3
Calcium...............	6.087	Argon........	15.1
Magnesium..	7.613	Oxygen...............	15.5
Thallium......	7.3	Nitrogen.	16.9
Cadmium..............	8.955	Helium...............	25.6

[1] FOOTE and MOHLER, "The Origin of Spectra," Chemical Catalog Company, Inc., New York, 1922.

sodium.   Again, comparing oxides with platinum at the same temperature, the current from the former is far the greater, being even 1,000 times that of platinum in many cases.   A rise of temperature causes a rapid increase in current.   In vacuum, platinum at 1357° will produce a current of the order of 10^{-8} amp per cm^2, although at 1500° the emission is nearly 100 times as great.

Certain gases, especially hydrogen, have a stimulating effect upon thermionic emission.   As an example, the current from platinum at 1350° is 2,500 times greater in an atmosphere of hydrogen at 0.0006 mm mercury pressure than in vacuum.

Thermionic discharge has found extensive application, by means of the audion or radiotube, in the amplification of currents set up in wireless receivers.

The gases issuing from a flame, as well as the flame itself, will conduct electricity.   Suppose two pieces of metal to be placed in a bunsen flame and one of them raised to a moderately high potential.   A weak current which is practically independent of the distance between the two metals will flow.   Conducting ions are present in gases of the flame.   The strength of the discharge increases with the temperature of the flame and with the potential, showing no sign, however, of reaching saturation value.   It will be found that the electric field is much stronger near the

negative electrode than elsewhere in the flame. The resistance to the current, therefore, is largely centered at this point.

The presence of salts, particularly those of the alkali metals, in the bunsen flame strengthens the current, the amount depending upon the nature of the metal of the salt. It is believed[11] that the salt, converted into metallic vapor, partially dissociates into metallic ions and electrons, thus causing the increased conductance. According to Moreau,[12] the electrons where the electric field is strong collide with vaporized alkali-metal atoms, thus causing ionization. The most appreciable effect of the salt is obtained if the negative electrode be coated with it, inasmuch as the greatest resistance to the passage of the current occurs at that locality. Increases as high as a thousandfold may result with no change in the potential difference between the electrodes. Coating the negative electrode with a salt and applying an alternating emf will result in the passage of a large current through the flame. If the positive electrode be coated instead, the flow will be small. Hence the current is in effect limited to one direction.

Ionization and Chemical Reaction. In electrolysis, electrochemical activity and the separation of products occur entirely at the electrodes, the chemical action being a necessary consequence of the liquid-solid boundary existing there.[13] In an electrical discharge through gases, however, ionization and recombination of ions take place throughout the gas rather than at the electrodes. The accompanying chemical action is therefore not simple. It bears a relation to ionization but not directly to the current, according to Lind.

The chief progress in the study of chemical action in the flow of current through gases has been made at low pressures, for little is known regarding ionization at high gas pressures. Lind holds that the electrochemistry of gases is far more important in the latter region, which warrants continued investigation.

The small number of molecules ionized during the passage of an electrical discharge through a gas are in a chemically active state. In electrical discharge tubes, diatomic molecules of the inert gases and their compounds with hydrogen are shown to

[11] WILSON, H. A., *Trans. Am. Electrochem. Soc.,* **44,** 127 (1923).

[12] MOREAU, G., *Ann. chim. phys.,* **24,** 289 (1911).

[13] LIND, S. C., *Trans. Am. Electrochem. Soc.,* **44,** 63 (1923).

exist. Furthermore, the gaseous ions are the intermediate activated products of reaction, as may be seen in the production of CO_2 in ionized CO, where two molecules of CO are decomposed for each molecule of the gas ionized. The following equations show the reaction:

$$CO^+ + CO = (CO)_2^+$$
$$(CO)_2^+ + \ominus = CO_2 + C$$
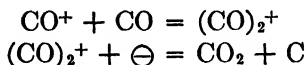
From these studies Lind[14] derives several general laws as follows:

1. Free electrons will play a primary role in promoting chemical reaction of gases only when a gas is present capable of forming a negative ion by attaching the free electrons. A secondary role is always played by electrons in restoring final electrical neutrality.

2. Gas ions tend to form charged complexes by attaching themselves to electrically neutral molecules. These complexes are the intermediate compounds of chemical reactions.

3. Activated molecules or atoms do not interact among themselves, but react with the unactivated molecules.

4. Ineffective encounters may destroy the activity of one of the components by leading to the reverse reaction.

When an electrical discharge passes through air, the resultant chemical action produces ozone and nitric oxide. As the temperature rises, there will be an increase, not only in the proportions of these compounds in the equilibrium gas mixture, but also in their rate of decomposition. Ozone decomposes at 200° and nitric oxide at 1200°C. Hence the concentrations of these gases will be governed by the temperature as well as the rapidity with which they move away from the high-temperature zone. In the flaming arc and spark discharge, nitric oxide alone results; in the brush discharge, both gases are formed; while in the dark discharge, ozone is produced with but very little nitric oxide.

A study of the disappearance of gases in discharge tubes has shown that such disappearance or "cleanup" does not occur unless the potential applied to the electrodes be great enough to ionize the gas. It is therefore concluded that the disappearance is due, not to any direct chemical action, but to the electrical discharge itself. In general, the rate of cleanup is directly

[14] *Ibid.*

proportional to the ionization.[15]   It is furthered by the deposition
on the cathode of the discharge tube of such substances as phos-
phorus, sulfur, iodine, arsenic, sodium, and potassium.   The first
three are the most effective in the rapid removal of hydrogen and
nitrogen, the lowest final pressure being reached with phosphorus
and sulfur.[16]

The Research Laboratories of the General Electric Company
have devoted much time to the investigation of these reactions,
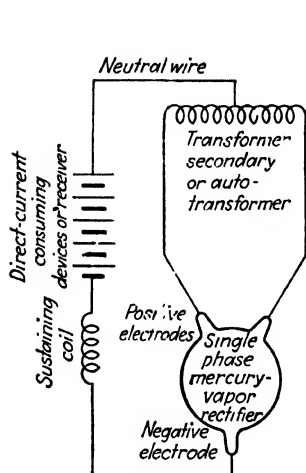
Fig. 248.   Single-phase mercury-
vapor rectifier.
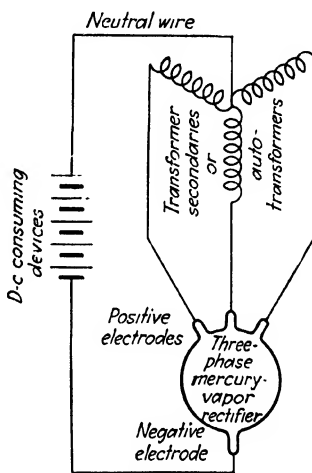
Fig. 249.   Three-phase mercury-
vapor rectifier.

the cleanup being involved in the manufacture of electric incan-
descent vacuum lamps, X-ray tubes, and the like.

Mercury-arc Rectifiers.   This mechanism is an electric valve
which allows current to flow only from a positive terminal to a
pool of mercury.   As long as the terminal has a critical potential
above the mercury electrode, current will pass, but the moment
the potential falls below the critical, the current decreases, rapidly
dropping to a zero value.

In small sizes the construction is simple, consisting of an
evacuated chamber with a pool of mercury (termed "cathode")

[15] Research Staff of the General Electric Company, Ltd. (England), *Phil.
Mag.*, **40**, 585 (1920).

[16] NEWMAN, F. H., *Trans. Am. Electrochem. Soc.*, **44**, 77 (1923).

connected to a terminal and a pair of electrodes in the one-phase arc, three electrodes in the three-phase form (termed "anodes") of iron or graphite inserted through the walls of the chamber. Figure 248 diagrammatically shows the arrangement for a single phase and Fig. 249 for a three phase with three anodes. Rectification curves for the one- and three-phase types are given in Figs. 250 and 251. The mechanism is started through an
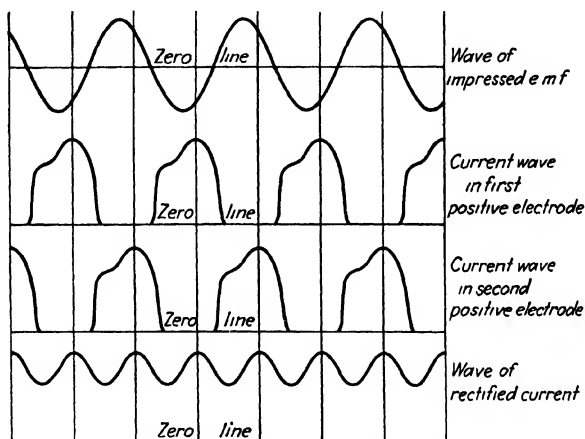
FIG. 250. Typical wave form of single-phase rectifiers.
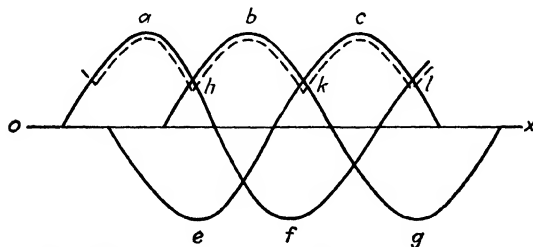
FIG. 251. Typical wave form of a three-phase rectifier. Curves *a*, *b*, and *c* are the successive voltage waves of a three-phase system. The current in the secondary circuit connected to the rectifier will flow first from the phase *a* to the cathode, thence through the d.c. circuit back to the neutral point of the three-phase system. This current will continue until the point *h* on the curve *a* is reached, at which there will be transference to the anode connected to the *b* phase, when the current will follow the dotted line from the point *h* to the point *k*, where there will be transference to the *c* phase, and current will follow the dotted line from *k* to *l*. The dotted line is the cathode potential in reference to the neutral point of the three-phase system, which in turn is the positive terminal of the direct current supplied by the rectifier whose potential is represented by the line *ox*.

auxiliary device, but it is self-sustaining under load. The source of electrons is the hot spot in the pool of mercury, the necessary heat being produced by positive-ion bombardment. The "space charge" effect of the electrons is reduced by the positive ion, and the voltage drop across the tube is held to a value low enough to permit good voltage regulation. Inasmuch as only one of the electrodes is hot, it is the sole source of electrons. Thus when alternating current is applied across the terminals, the current flow will be unidirectional direct current. In operation the electrons which are liberated proceed at high velocity toward the anode and ionize molecules of gaseous mercury. Positively charged bodies are produced, and the stream of electrons moving toward the anode is thus increased, while the positively charged bodies are drawn toward the cathode. Here they become neutralized or negatively charged and thus further increase the ionization at the cathode. A potential gradient is set up which accelerates electron emission. The rectifying power depends upon the extent of the Crookes dark space. Inasmuch as the volume of this space grows greater with decrease of pressure, it is desirable to keep vapor pressure and temperature low.

In connection with power-type mercury-arc rectifiers, Remscheid[17] discusses the chemical and electrical engineering difficulties.

The evolution of the rectifier, from the two-anode glass-bulb type of comparatively low current rating to the modern high-current steel-tank multiple-anode type, has required much research into the fundamentals of mercury-arc phenomena. Other major problems have been of a mechanical nature such as: the design and production of a steel chamber which may be operated at vapor pressures of $\frac{1}{10}$ of a micron (1/7,600,000 part of an atmosphere); high-speed self-leveling mercury-condensation vacuum pumps, capable of producing and maintaining such a vacuum; a small rotary air pump capable of continuous operation; adequate insulating seals for anode conductors entering the vacuum chamber, capable of withstanding high temperatures; the production of a vitreous-enameled steel, cathode-to-tank insulator, suitable gasket material, preferably of a nonorganic nonoxidizing nature; a means of preventing the corrosion of the water-cooled parts, etc.

The energy loss of power rectifiers which is liberated in the form of heat has been removed by several methods such as air blast, circulating

[17] REMSCHEID, E. J., *Gen. Elec. Rev.*, **41**, 550 (1938).

water, and direct radiation. For modern high-power steel-tank rectifiers, the closed water-cooling system (using a corrosion-inhibiting solution) has been intensively developed and is almost universally used at the present time.

During the phenomenon of rectification, mercury is boiled away from the cathode at the rate of approximately 0.8 g per sec per 100 amp of cathode current, the mercury vapor is condensed, and the liquid mercury is returned to the cathode pool. Condensation takes place on the cooled side walls of the rectifier, thus transferring the heat to the cooling medium. The temperature control region of modern high-power rectifiers is the projected area under the anodes. The cooling system, in addition to condensing the mercury vapor and removing the heat losses generated in the rectifier, regulates the mercury-vapor pressure within definite limits.

The rather complicated construction of a power rectifier is shown in Fig. 252.

In the ignitron type of mercury-arc rectifier, an essential feature is the igniter. When a small current, say of the order of 20 amp,[18] passes through a rod of silicon carbide or boron carbide dipping into a mercury pool, a cathode spot develops immediately at the rod-mercury junction. The ignitron consists of an evacuated chamber with a mercury pool at the bottom, into which dips the graphite rod serving as the igniter. Construction of a typical commercial form is shown in Fig. 253.

Gaseous Electrothermics. One of the major applications of electric arcs in connection with chemical reactions is in the fixation of nitrogen. At the present time the fixation of atmospheric nitrogen by electrical discharge does not exist as an industry in the United States. Its very high power consumption, which is of the order of 67,000 kwhr per metric ton of nitrogen, has caused it to be confined to countries where unusually cheap power is available, a situation existing only in Norway. A tremendous amount of experimental development and plant work has been expended in connection with the problem. As far back as 1902 the Bradley and Lovejoy process was installed at Niagara Falls. They employed an apparatus which produced a multitude of thin arcs. These were rapidly extinguished and restarted. Their fundamental idea was that as much air should come under the influence of the discharge as possible, and gases

[18] SLEPIAN, J., *Trans. Electrochem. Soc.*, **69,** 339 (1936).
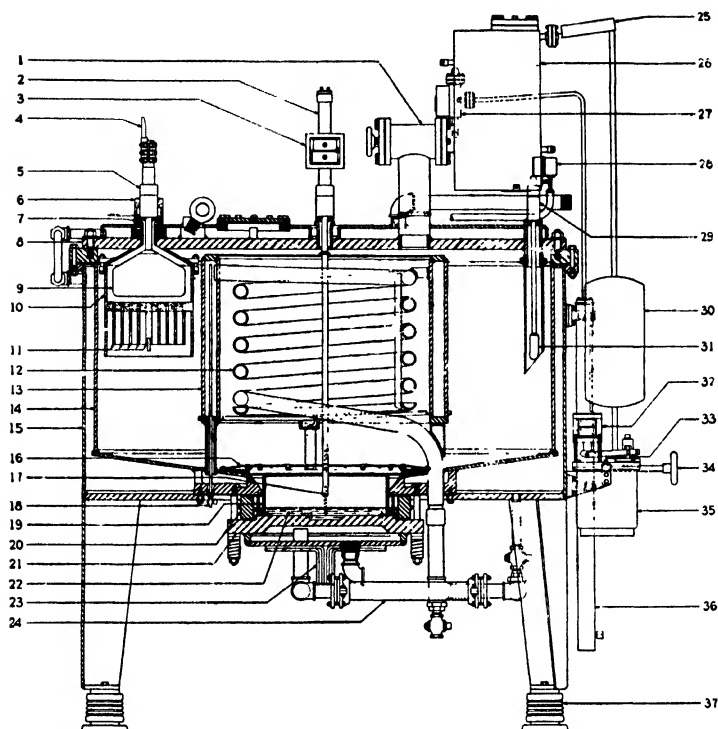
FIG. 252.   Sectional view of 3,000-kw, 600-volt mercury-arc power rectifier.
(*General Electric Company.*)

1. Manual vacuum valve	20. Cathode insulator
2. Starting anode armature sleeve	21. Cathode plate
3. Starting anode solenoid winding and yoke	22. Cathode mercury
	23. Cathode terminal
4. Main anode terminal	24. Cathode insulating pipe
5. Main anode insulating seal	25. Air-cooled mercury trap
6. Main anode heater cover	26. Mercury condensation pump
7. Main anode heater	27. Vacuum detector
8. Tank cover plate	28. Thermal relay for mercury condensation pump
9. Main anode tip	
10. Baffle cylinder	29. Excitation-anode insulating seal
11. Baffle	30. Gas receiver tank
12. Internal cooling coil	31. Excitation anode tip
13. Internal cooling cylinder	32. Rotary pump valve solenoid
14. Vacuum tank	33. Rotary pump valve
15. Water jacket	34. Vacuum gage operating hand-wheel
16. Mercury separator	
17. Starting anode tip	35. Rotary vacuum pump
18. Air vent	36. Vacuum gage
19. Quartz arc shields	37. Rectifier insulators

should be cooled very quickly. Gases containing **2** to **3** per cent NO were produced with a HNO_3 yield of 86 g per kwhr. The largest unit built was 10 kw.

A second and somewhat more successful attempt to establish the arc process in the United States was that of the Southern Electrochemical Company at Nitrolee, S.C., in 1913, employing
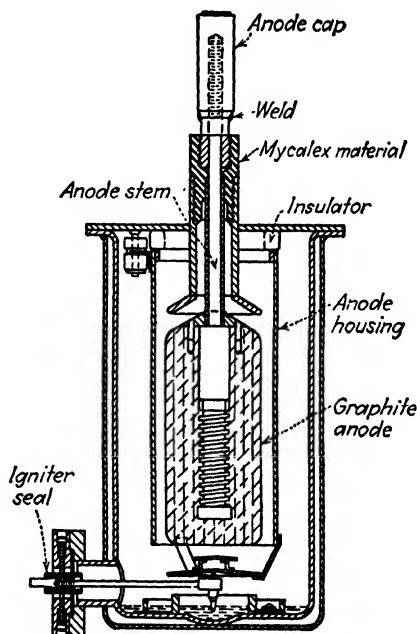
Fig. 253.   General Electric ignitron-type mercury-arc rectifier, 300 kw, 275 volts. (*General Electric Company.*)

the Pauling process. Power at 0.153 cent per kilowatthour was available, but the energy consumption of 19,500 kwhr per ton of HNO_3 rendered operation uneconomical, with the resultant closing down of the plant in 1916. In 1917 an arc-process plant was erected by the American Nitrogen Products Company at Le Grande, Wash., using the Wielgolaski furnace. This unit contained two or more chambers shaped like an inverted U, the electrodes being placed between the ends of the limbs of the U and a long U-shaped arc caused to spring between them. The electrode consisted of a water-cooled pipe bent into a ring, and

the air was blown through the ring.   The plant is no longer in operation.

At the present time only the Birkeland-Eyde and the Schönherr-Hessberger processes are in operation in Norway.   Pauling plants built and operated in various European countries are no longer in use.   It is estimated that in recent years there has been a capacity of about 46,500 tons of nitrogen in arc-process plants with actual production of the order of 30,000 tons.   This is only a very small percentage of the total synthetic nitrogen production, being far smaller than the production by any other commercial process such as NH_3 synthesis or cyanamide.

Fixation of Nitrogen by Electric Arcs.   The formation of nitrogen oxides at a high-tension arc discharge in air was first
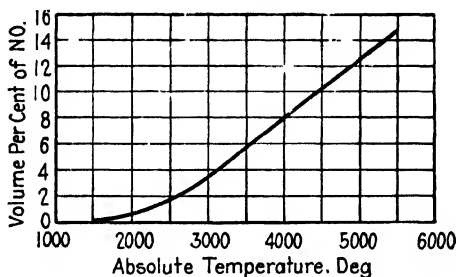
Fɪɢ. 254.   Equilibrium concentrations of NO in air at various temperatures.

noted by Crookes, although Rayleigh[19] was the first to study the process from the commercial point of view and the production of HNO_3.   The equilibrium concentrations of NO in air at different temperatures were experimentally determined by Nernst, Jellinek, and Finckh.[20]   Their results are plotted in Fig. 254.   A number of theories have been proposed such as the thermal one in which the formation of oxides of nitrogen was presumed to be a function of temperature.[21]   At low temperatures NO is unstable, its equilibrium concentration in the presence of N and O being very small.   The reaction is given as $N_2 + O_2 = 2NO - 43,100$ cal at room temperature.   Higher temperatures should thus favor the formation of NO.   According to the thermal theory,

[19] Rᴀʏʟᴇɪɢʜ, J. W., *Trans. Chem. Soc.* (London), **71**, 181 (1897).

[20] Nᴇʀɴsᴛ, W., Jᴇʟʟɪɴᴇᴋ, K., and Fɪɴᴄᴋʜ, K., *Z. anorg. Chem.*, **45**, 116 (1905); **49**, 213, 229 (1906).

[21] Mᴜᴛʜᴍᴀɴɴ, W., and Hoғᴇʀ, H., *Ber.*, **36**, 438 (1903).

the incoming gases are heated to the temperature of the arc and NO is produced at the concentration in equilibrium with N_2 and O_2. The gaseous mixture passing out of the arc zone is cooled, during which time there is a tendency for the NO to decompose according to the equilibrium concentration at lower temperatures. It would follow that it is desirable to have a high temperature in the arc followed by a very rapid cooling of the gases. Haber and Koenig[22] showed, however, that electrical phenomena can play a very important part and that under certain circumstances thermal effects are of a secondary nature. Their experimental work showed that the thermal theory was inadequate. Steinmetz[23] suggested the theory that NO formation was due to the union of nitrogen and oxygen atoms which were produced by dissociation in the powerful electric field in the arc rather than by thermal dissociation.

The designers of nitrogen-fixation furnaces tried to get very high temperatures in the arc with sudden cooling. It was soon found, however, that the NO concentration did not increase as quickly as did the consumption of electrical energy in a given space but soon reached a limit where any further increase in energy was useless. Thus short thick arcs were avoided and many devices proposed for the maintenance of long thin stable arcs with which a large quantity of air could be brought into contact.

Birkeland-Eyde Process. In the Birkeland-Eyde process an a.c. arc is sprung between electrodes in a powerful electromagnetic field with the resultant formation of a disk type of discharge. The arrangement permits a great concentration of power in a given space, as well as the introduction near the electrodes of air which can be passed through the arc, be fully exposed to its action, and be removed at the periphery of the disk discharge. A typical arc formation is shown in Fig. 255. In a typical unit the
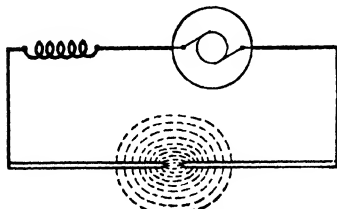
Fig. 255.   Birkeland-Eyde arc.

[22] Haber, F., and Koenig, A., *Z. Elektrochem.*, **13**, 725 (1907); **14**, 689 (1908); (with Platou, E.) **16**, 798 (1910).

[23] Steinmetz, C. P., *Chem. & Met. Eng.*. **22**, 299, 353, 411, 455 (1920).

electrodes are 5-cm (1.97-in.) water-cooled copper tubes bent in the form of a narrow U and placed about 1 cm (0.4 in.) apart. The arc, whose temperature is estimated at 3200°C, burns vertically through holes in a brick-lined furnace, in the steel shell of which air enters. A 750-kw unit has a furnace chamber about 5 ft high, 5 ft wide (corresponding to the dimensions of the disk), and 2 to 6 in. deep in the direction of the magnetic field. Two electromagnets are connected to the external casing and take 0.35 to 1 per cent of the total load. A typical unit is shown in Fig. 256. About 5,000 volts is required, of which 3,300 to 3,900 are across the arc, the remainder being consumed in the series inductances. Power factor at 60 cycles is 66 to 68 per cent at currents of 190 to 200 amp. Larger units of 3,200 to 4,000 kw of 80 per cent power factor, employing three-phase current and three delta-connected furnaces, have been built. Furnace gases contain about 1.25 per cent NO at 900 to 1000°C at the furnace exit. The energy consumption is 15,000 kwhr per metric ton of HNO_3 or 67,000 kwhr per metric ton of nitrogen.

FIG. 256. Sectional elevation of Birkeland-Eyde furnace at right angles to arc disk.

It is stated that the electrodes last 400 to 500 hr and furnace linings 4 to 6 months.

The Birkeland-Eyde electric arc process for the fixation of atmospheric nitrogen yielded an effluent gas containing from 1.0 to 1.5 per cent of nitric oxide and a yield equal to about 61 to 63 g of nitric acid per kilowatthour. It is understood that a modification of the process has been made to yield as high as 80 g of nitric acid per kilowatthour.

Cotton[24] described a process which can be made to yield an effluent gas containing as high as 25 to 30 per cent of nitrogen oxides and the yield in terms of grams of nitric acid per kilowatthour equal to 10 to 15 times, and in some instances as high as

[24] COTTON, W. J., *Trans. Electrochem. Soc.*, **91**, 407–417 (1947).

20 times, that of the Birkeland-Eyde process, employing a crossed discharge.

Pauling Method.   In the Pauling process the arc was formed between two horn electrodes and preheated air blown up through a nozzle at the base of the arc, deforming it to a flame as shown in Fig. 257.   The electrodes were hollow water-cooled cast-steel members, about 30 cm (11.8 in.) long.   Electrodes were provided with vertical slits at the lowest point, through which passed thin knives whose distance apart could be regulated. These strips or knives were so thin that they did not affect the current of air and were used to start the arc.   The electrode life was very short, being 200 working hours for the main electrodes and 20 hr for the thin strips.   In the industrial units a 600-kw furnace contained two 300-kw arcs in series at a total voltage of 5,000, current of 200 amp, and power factor of 60 per cent.   Furnace gases contained 0.08 per cent NO at 1000°C at the furnace exit, and energy consumptions were 16,800 kwhr per metric ton of HNO_3 or 75,500 kwhr per metric ton of nitrogen.
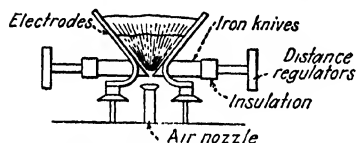
FIG. 257.   Pauling arc and electrodes.

Schönherr-Hessberger Process.   In the Schönherr-Hessberger process very long arcs are used in which the air current draws the arc out from a short to a great length.   Air is introduced not at right angles as in the Pauling furnace, but so that it surrounds the arc and travels along parallel to it.   Air comes in contact with the electrical discharge by diffusion and eddy currents from all sides without deformation or undue cooling of the arc.   A typical furnace is illustrated diagrammatically in Fig. 258.   The arc chamber consists of a vertical iron pipe serving as one electrode which is grounded.   It is 20 to 25 ft long, a few inches in diameter, water-jacketed at the top, and slightly belled at the bottom, into which end the other electrode, carefully insulated from it, fits vertically.   This lower arc terminal is a rod of iron connected to a water-cooled copper block and can be raised and lowered.   The arc chamber is surrounded by other concentric vertical iron tubes, which in turn are surrounded by a firebrick furnace chamber in a steel shell.   Air enters at the bottom of the furnace, travels vertically upward through one of

the iron pipes to the top, then passes downward in the pipe sur-
rounding the discharge chamber where it is preheated. The air
enters the discharge chamber near the bottom electrode, rises
vertically through it to the top of the fur-
nace, and again passes downward alongside
the firebrick lining. Here it gives up some
of its heat to incoming air in the adjacent
tube, and leaves the furnace at the bottom.
In operation an arc is started between the
lower terminal and the wall of the discharge
chamber and is lengthened out as a result
of the action of the incoming air, which
ascends the discharge chamber with a hel-
ical motion. The length of the arc is a
function of the applied voltage and the
conductivity of the gases. This in turn is
a function of temperature which again is a
function of the air velocity and the effec-
tiveness of the heat interchange between
the gases leaving the furnace and those
entering it. Stable arcs some 20 ft long
are thus produced between the lower term-
inal and some point in the top of the dis-
charge chamber where it is water-jacketed.
Typical furnaces are three phase, three
single-phase units being connected in star,
and take loads of 750 to 1,000 kw at 350
volts and 290 amp. Series inductances
are used to stabilize the arc. Power fac-

FIG. 258. Schönherr-
Hessberger furnace.

tors are around 66 per cent. The gases contain 1.8 per cent
of NO at 1200°C at the discharge chamber exit and 850°C
at the furnace exit. Entering air is warmed to 500°C by heat
interchange. Energy consumption is of the order of 14,800
kwhr per metric ton of HNO_3, or a little less than 67,000 kwhr
per metric ton of nitrogen. Schönherr calculates that only 3 per
cent of the total energy of the furnace is used in the formation
of nitrogen compounds. The first cost of plant as well as repair
and maintenance is relatively low.

The Schönherr-Hessberger and the Birkeland-Eyde units show
yields which are almost identical, but the former gives a gas

having a higher content of oxides of nitrogen and in addition is of simpler construction, more durable, and lower in first cost. On the other hand, the Birkeland-Eyde furnaces can be built in larger sizes. The simplicity of the Pauling apparatus is offset by the very dilute gases produced, as well as the small size of the units. Both the Birkeland-Eyde and the Schönherr-Hessberger furnaces have found satisfactory industrial application in Norway.

The gases containing the oxides of nitrogen are cooled by heat-interchange methods, first in waste-heat boilers and then in coolers where their thermal energy is used to preheat air, and are worked up in absorbing towers into HNO_3 or $Ca(NO_3)_2$ or both. In earlier plants $NaNO_2$ was also produced.

Hydrogen Peroxide by Electric Discharge. Since 1931 the Elektrochemische Werke had worked on the development of a process for the direct synthesis of hydrogen peroxide from hydrogen and oxygen. Units of 10, 20, and 10,000 watts had been constructed and calculations completed for a 2,000,000-watt unit. This method has the advantages of a pure product and relatively little labor since the controls of the apparatus are automatic.[25]

The cyclic process based on the combining of hydrogen and oxygen can be explained by reference to Fig. 259. Oxygen, hydrogen, and steam were mixed at a little more than atmospheric pressure by blower A and were then forced through a heat exchanger to the ionizing chamber B. Owing to the electric discharge here, part of the hydrogen was atomized and ionized. The ionizing chamber B was made of a number of parallel quartz plates 5 mm thick and 500 mm square, one side being etched with hydrofluoric acid and the other side having electrically connected aluminum coatings. The plates were connected electrically in parallel and were separated by 5 mm from each other with the etched sides facing. Twelve thousand volts of 9,500-cycle alternating current was used with a working density of 0.96 kw per pair of plates. The gas mixture in the ionizing chamber had a water vapor pressure corresponding to water at 60°C and the average temperature of the gases was 160°C. The hydrogen peroxide formed in the ionizing chamber was swept out with the other gases through a heat exchanger to the rectifying column containing Raschig rings. A condenser E was at the top of the column, and at point F distilled water

[25] U.S. Patent 2,015,040 (to Elektrochemische Werke).
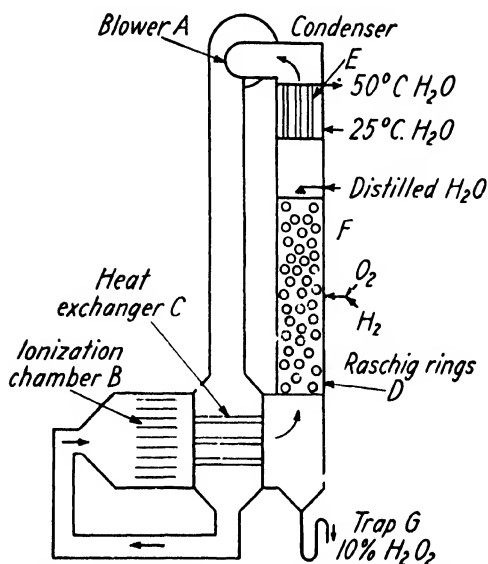
Fig. 259. Unit for production of H_2O_2 by electric discharge.

was introduced. From trap G a very pure 10 per cent solution of hydrogen peroxide flowed. The necessary hydrogen and oxygen were introduced at point H. Automatic controls were used so that the oxygen content was maintained at 5 per cent with very little labor. The energy efficiency was such that the equivalent of about 25 g of 100 per cent hydrogen peroxide was produced per kilowatthour.

CHAPTER 26

ELECTRONICS

In a metallic conductor there is a continual interchange of electrons between adjacent atoms, and there are always a number of free electrons, each one of which is free for only a short time. If a potential be applied to the conductor, a current is produced as a result of the movement of the free electrons in the conductor toward the positive pole or point of higher potential. The free electrons in a metal are considered to be in constant motion with an average velocity which is directly proportional to temperature. The surface of the conductor is impervious to most of the electrons at normal temperature. If the conductor be heated, a large number of electrons are able to break through the surface into the surrounding space. In a gas under normal conditions there is no interchange of electrons and no conduction. If the temperature of the metallic conductor be sufficiently high, it will not hold an electric charge but will give off electrons or thermions. The electric current from such a body is called a "thermionic current."[1]

Vacuum Tubes. The vacuum tube makes use of thermionic discharge. In its simplest form the device consists of a highly evacuated glass bulb containing an anode or plate and a metallic filament of tungsten or other metal which may be electrically heated. A diagrammatic sketch of a two-element tube is given in Fig. 260. If the switch be open, there will be no current through the ammeter; but if it be closed, a current will pass through the ammeter in the direction of the plate. This current is caused by electrons thrown off by the heated filament. They pass from the filament to the plate to produce an electric current in the circuit connecting the· filament and the plate. Only a few of the electrons given off by the filament reach the plate and most of them return to the filament. The current is, therefore, very small. Electrons which fill the space produce a negative

[1] Refer to previous chapter.

space charge which repels the electrons just leaving the filament and drives them back.   If a potential be applied to the plate (by an external source of current) to make the plate positive, the negative space charge is neutralized by the positive charge on the plate, and the electrons can leave the filament more readily.   In addition, positive plate charge tends to attract the electrons. As a result, a larger number leaving the filament reach the plate, and the current in the circuit is greatly increased.   The thermionic currents produced even in this case are small.   Vacuum
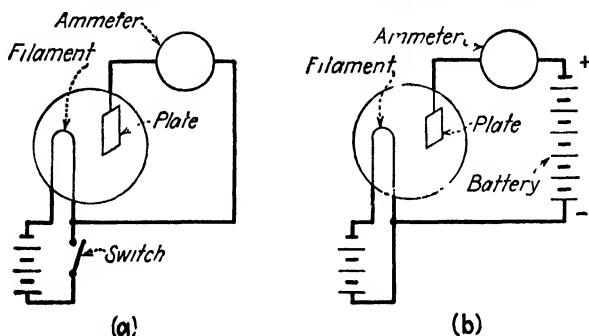
FIG. 260.   A two-element electron tube.

tubes commonly used in radio-receiving sets have currents ranging from 1 to 2 milliamp to about 25 milliamp, while those employed as rectifiers pass as much as 5 or 6 amp.   If the plate, as the result of reversal of the polarity of the external source of current, be made negative, the plate would acquire a negative charge which would increase the negative space charge and drive the electrons back to the filament.   If the external source be an alternating current, the plate will be alternately positively and negatively charged, and the tube could be employed as a rectifier.

It has been previously shown that thermionic emission is a function of the electrode material, the temperature, and the nature and pressure of the surrounding gas.   Certain gases have a stimulating effect upon thermionic emission.   If a gas at a low pressure be introduced into the vacuum tube described above, the current through the plate may be increased as the result of ionization of the gas and neutralization of the negative space charge.   Vacuum tubes employing ionized gas are extensively used as rectifiers.

As long as the potential applied to the plate and the heating

current in the filament circuit are both constant, a steady current
will flow through the tube circuit. The relation between plate
potential and current in the plate circuit is given in Fig. 261.
At first, increase of plate potential increases plate circuit current
until a constant or saturation value is reached at which further
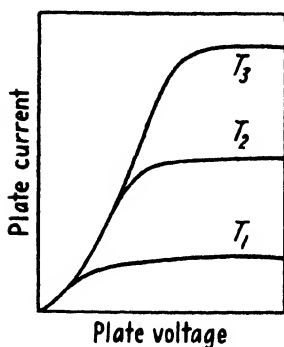
increases of plate potential do not
increase plate current. If the tem-
perature of the filament be raised
through increase of filament current,
this saturation value will be in-
creased. Saturation occurs when
all the electrons emitted by the fil-
ament are attracted to the plate.

The amount of current in the
plate circuit may be varied by the
insertion of a third element called
the "grid," consisting of a fine wire,
wound around suitable supports,
with the turns spaced a considerable
distance apart. Electrons reaching
the plate therefore have to pass

through the meshes of this grid. If the tube be operated
at such a value of plate potential and filament current that
the plate current is well below saturation, the grid potential
with respect to the filament is zero. If a negative potential
be applied between the grid and filament, the current in the
plate circuit will decrease, and if sufficient negative poten-
tial be applied to the grid, the plate current may be stopped
entirely. If the grid be made positive with respect to the fila-
ment, the plate current will increase. Under such a condition
not all the electrons will reach the plate, in that some are attracted
to the grid and a grid current flows from the filament to the grid.
A three-electrode tube (Fig. 262) then becomes an electron relay
and permits the control of a large plate current by means of a
small potential applied to the grid. With a fixed grid potential
the current in the plate circuit increases with increase of plate
potential until saturation is reached.

Four-element tubes, with two grids instead of one, have advan-
tages for certain applications. Many modifications of grid tubes
have been developed. They have individual characteristics and

more or less specialized uses. The static characteristics of a three-electrode vacuum tube are shown in Fig. 263. Small changes in grid potential will produce a large change in plate current; hence the tube may be used as an amplifier for an emf
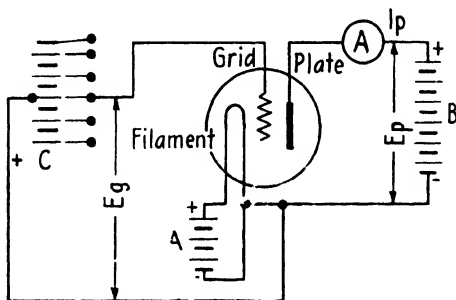
FIG. 262. Connections to show effect of change in grid voltage.

wave applied to its grid. When operated as an amplifier, changes occur in the plate current and in the energy in the plate circuit. This change of energy is much greater than the corresponding change in the grid circuit.

Three-element vacuum tubes may be made to oscillate by
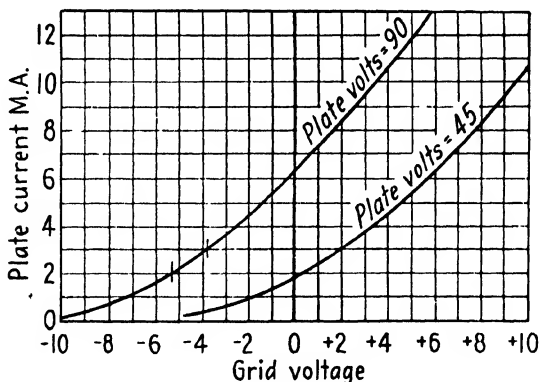
FIG. 263. Static characteristics of electron tube.

electrical arrangements which involve some method of introducing energy from the plate circuit into the grid circuit of the tube, with the production of alternating current of sine wave form over an extremely wide range of frequencies. These oscillators are the most common source of energy for radio communi-

cation. By other arrangements the three-element vacuum tube
may be used as a modulator or a detector for radio signals.

Photoelectric Tubes. The photoelectric tube is based on the
property of certain metals, such as Na, K, Rb, Ca, Cd, Se, or Ce,
giving off electrons when they are exposed to ordinary light.
A photoelectric tube may be constructed by coating a portion
of the inside of an evacuated glass bulb with a layer of the metal
and connecting this as one terminal of the circuit, with a metal
electrode placed inside the bulb near the coated surface as the
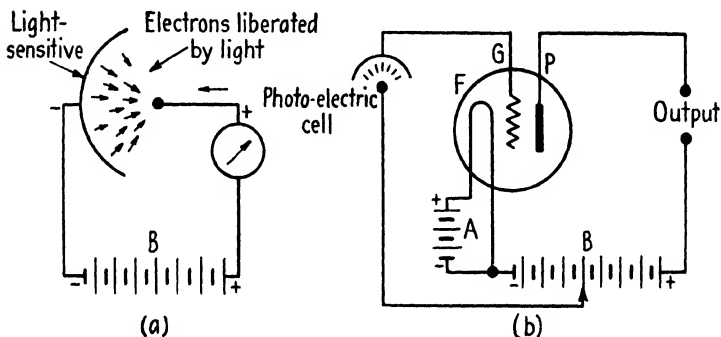
Fig. 264.   Amplification of photoelectric tube current.

other terminal. As long as light falls on the photosensitive
metal layer, a current will flow, the strength of which will be
dependent upon the intensity of the light.   The current ordi-
narily produced is very small and may be amplified by the use
of a three-element vacuum tube as shown in Fig. 264.   The
metallic coating on the glass may be replaced by a plate of the
photosensitive metal.   High-vacuum photoelectric tubes have
a high voltage drop and require a high polarizing potential.
This can be reduced if gas at a low pressure be used in the tube,
with a decrease, however, of permanence of the characteristics
of the unit.   Both types of tubes are employed for purposes
such as television for the transmission of photographs or copy
by radio or wire lines.   They are finding a wide variety of appli-
cation in manufacturing industries for inspection, for sorting
of products which vary in color, for the detection of smoke, as
guards on machines where a continuous ray of light is directed
on the tube and any object which cuts off the light makes the
machine inoperative, as well as other purposes where a variation
of light is to be detected.

Photovoltaic Cells. Photovoltaic cells are devices containing two electrodes immersed in a suitable electrolyte, between which electrodes an emf is produced or a change of emf effected when electromagnetic radiation such as light is incident on the photoactive elements of the cells. An example is a cell of the type $Cu:Cu_2O$ as one electrode, $Pb(NO_3)_2$ as the electrolyte, and Pb as the other electrode. This cell has the sensitivity of 150 microamp per lumen.[2]

Electronic tubes may be used as potentiometers, particularly in connection with the glass indicator electrodes for acidity control where the hydrogen, quinhydrone, and metallic electrodes cannot be used because of rapid poisoning.[3] New units are constantly being developed and new applications found.

New developments of electronic devices and applications of vacuum tubes and photoelectric cells are constantly taking place. For these the reader should refer to the current literature.[1]

GENERAL REFERENCES

THERMIONIC TUBES:

MORECROFT, J. H., "Electron Tubes and Their Applications," John Wiley & Sons, Inc., New York, 1933.

KOLLER, L. R., "The Physics of Electron Tubes," McGraw-Hill Book Company, Inc., New York, 1934.

HENNEY, K., "Electron Tubes in Industry," 2d ed., McGraw-Hill Book Company, Inc., New York, 1937.

KLOEFFLER, R. G., "Principles of Electronics," John Wiley & Sons, Inc., New York, 1942.

FINK, D. G., "Engineering Electronics," McGraw-Hill Book Company, Inc., New York, 1938.

MAXFIELD, F. A., and BENEDICT, R. E. R., "Theory of Gaseous Conduction and Electronics," McGraw-Hill Book Company, Inc., New York, 1941.

COBINE, J. D., "Gaseous Conductors," McGraw-Hill Book Company, Inc., New York, 1941.

PHOTOELECTRIC CELLS:

CAMPBELL, N. R., and RITCHIE, D., "Photoelectric Cells," Sir Isaac Pitman & Sons, London, 1929.

HUGHES, A. L., and DuBRIDGE, L. A., "Photoelectric Phenomena," McGraw-Hill Book Company, Inc., New York, 1932.

ZWORYKIN, V. K., and WILSON, E. D., "Photocells and Their Application," John Wiley & Sons, Inc., New York, 1932.

[2] FINK, C. G., and ALPERN, D. K., *Trans. Am. Electrochem. Soc.*, **58**, 275 (1930).

[3] PARTRIDGE, H. M., *Electronics*, **1**, 166 (1930).

[4] *Electronics*, beginning with Vol. 1 in 1930, published monthly by McGraw-Hill Publishing Company.

Part VI
ENGINEERING

CHAPTER 27

MATERIALS OF CONSTRUCTION

Materials of construction for electrochemical apparatus may in general be subdivided into three classes: those employed in electrolytic cells in which aqueous electrolytes are used, those finding application in fused electrolyte work, and those in electrothermic operations. In the first, the portions of the cell to be considered are the anodes, cathodes, diaphragms, and tank materials; in the second, electrodes, containers, and their linings; in the third, the electrodes, the containing body of the apparatus, and the lining.

Anodes for Aqueous Solutions. At the present time graphite serves as anode in chlorine and chlorate cells and in the production of magnesium and sodium metals. Graphite is very slightly attacked by chlorine, while amorphous carbon shows appreciable attack. Both graphite and amorphous carbon rapidly disintegrate in acid solutions, particularly those containing H_2SO_4. In salt electrolysis it has been found advantageous to increase the anode life by impregnating the graphite with a cobalt solution, as the result of which the anodic voltage can be reduced several tenths of a volt. Other methods have involved impregnating the anode with linseed oil or with synthetic plastics such as the phenol formaldehyde, resorcin formaldehyde, and chemically related products. Graphite and carbon are very useful as unattackable anodes in solutions which do not evolve much oxygen.

Lead has found wide use as an insoluble anode in the electrodeposition of metals in sulfate electrolytes not containing chlorides. In an alloy formed with silver in small amounts as the alloying constituent, it is employed in the electrodeposition of zinc from sulfate electrolytes. A whole series of lead alloys with Ag, As, Ca, Ba, Mg, Tl, Cd, and Bi have been tested and studied.[1] Anodes of 61 per cent Ag and 39 per cent Pb have been

---

[1] TAINTON, U. C., TAYLOR, A. G., EHRLINGER, H. P., *Trans. Am. Inst. Mining Met. Eng.*, 1929, p. 192; HANLEY, H. R., CLAYTON, C. Y., WALSH, D. F., *ibid.*, 1930, p. 275.

proposed for use in salt electrolysis for chlorine production.[2]   To increase the anode stiffness and mechanical strength, antimonial lead of various compositions has been recommended.   In some cases the antimony content has been as high as 40 per cent.   In use, the lead anodes become covered with PbO_2, so that the surface of a lead anode must be considered electrochemically as a PbO_2 electrode.   In the case of both the lead and the lead alloys, the solution must be free from ions, such as chlorates and nitrates, with which the lead would form soluble salts. Study of the anodic behavior of lead anodes has resulted in the development of a number of compositions that are resistant to anodic corrosion.[3]   Many of these have low oxygen overvoltage. Extensions of the theory of catalysis and the development of so-called "promoters" or "secondary catalytic substances" increasing the action of the original catalysts have been applied to the catalytic effect of films formed on anodes, particularly protective films resistant to anodic corrosion and having at the same time low oxygen overvoltage.[4]

Iron is the common anode and cathode material in electrolytic hydrogen-oxygen cells employing alkaline electrolytes.   When used as anode, the surface is generally coated with nickel to reduce the oxygen overvoltage, and as cathode in one cell the surface is coated with cobalt to reduce the hydrogen overvoltage, with resultant reduction of the total voltage across the cell. High-silicon irons such as Duriron were formerly used, in sulfate solutions containing small amounts of chlorides and nitrates, in copper extraction.   The anodes were brittle and corroded too rapidly, with the introduction of excessive amounts of iron into the solution.   For the same use fused magnetite electrodes were tried.   They were made of hollow castings, copper-plated on the inside to decrease the resistivity.   They were very brittle and showed appreciable corrosion in H_2SO_4 electrolytes, with the introduction of too much iron into the solution.

Platinum behaves satisfactorily as an insoluble electrode, but its use is very definitely limited by its cost.   It is employed only where other materials are so unsatisfactory that platinum

   [2] FINK, C. G., and PAN, L. C., *Trans. Am. Electrochem. Soc.*, **49**, 85 (1926).
   [3] FINK, C. G., and ELDRIDGE, C. H., *Trans. Am. Electrochem. Soc.*, **40**, 51 (1921).
   [4] FINK, C. G., *Ind. Eng. Chem.*, **16**, 566 (1924).

becomes essential. To minimize expense, the maximum possible surface must be obtained for a given weight so that various forms of gauze constructions are used in the production of perchlorates, perborates, and other peracids and persalts. In order to decrease overvoltage, platinized electrodes are preferable, but their use is limited by the fragile nature of the surface.

The concept of overvoltage of oxygen and the catalytic effect of the anode material have been of considerable industrial importance in the development of so-called "insoluble anodes" for industrial processes, particularly in the refining of metals.

Two of the reactions at the anode are of particular interest: (1) the combination of the anion with the metal of the anode, and (2) the discharge of the anions with the formation of gaseous oxygen. The relative velocity of these two reactions more or less determines the degree of solubility of the anode under the action of the current. It is not difficult to picture the ideal case for a perfect insoluble anode. The velocity of the second reaction is infinitely greater than that of the first reaction. The more we can catalyze the formation and evolution of gaseous oxygen, the more insoluble will be the anode.

In the electrowinning of copper an ideal anode would be of copper with a surface film that would catalyze the oxygen formation and evolution to such an extent that practically no copper of the anode would go into solution.

The Chilex insoluble anode, consisting mainly of copper silicide, was developed for copper electrowinning. Various addition materials are included to affect the films formed on the surface. The anode consists essentially of an alloy of copper, silicon, iron, and lead. In addition it has been found that a small amount of tin is beneficial, and for a time it was believed that the presence of about 4 per cent of manganese was desirable. On microscopic examination of etched specimens, the anode is seen to consist of two main constituents: one substance separated in primary crystals and very resistant to corrosion, and the other a binary or ternary eutectic mixture much more readily corroded. The primary crystals consist of free silicon, and the eutectic carries the rest including the lead and tin.

The behavior of the anode is similar to that of a storage-battery plate. The latter consists of PbO_2 particles, which

serve as current conductors to the solution, embedded in metallic lead, which serves as metallic conductor and current distributor and as the supporting grid to give mechanical strength. In the Chilex anode the eutectic has the same function as the PbO_2 produced from the lead in it by the oxidizing action of the current. The free silicon is the supporting grid and serves to protect the anode against too rapid mechanical and chemical corrosion.[5]

Cathodes for Aqueous Solutions. As cathodes, the number of materials needed is relatively few, in that in most cases, particularly in the refining of metals, the cathode sheet is made of the metal to be deposited. In the formation of starting sheets, lead and lead alloys are used for the "blanks" in copper refining. Aluminum which shows a high hydrogen overvoltage is employed in zinc electrowinning and was originally used in nickel refining, but was later replaced by stainless steels whose surfaces were more readily maintained. Stainless-steel cathodes of special composition are employed for manganese electrowinning. In copper, however, lead meets competition from copper blanks which are oiled or coated with a graphite wash. In nickel refining, aluminum blanks were generally given a Na_2S dip so that the starting sheet may be easily removed from the blank. In the production of chlorine and caustic in electrolytic cells, the common cathode materials are iron or steel whose use is almost universal. Alloys of iron with chromium and nickel, such as the stainless or corrosion-resistant steels not attacked chemically by nitrates or HNO_3, are employed as cathodes in the Moebius silver-refining cell. Cobalt-plated steel sheets serve as cathodes in the Levin hydrogen-oxygen cell. Copper gauze as cathode found application in the Hargreaves-Bird chlorine cell. Platinum, because of its high price, is used only to a limited amount in certain hypochlorite and persalt cells.

Diaphragms for Aqueous Solutions. The availability of suitable diaphragms frequently determines the success or failure of electrolytic processes. A good diaphragm must have sufficient mechanical strength and rigidity so that it may be kept in place without distortion or strain. It must be chemically resistant and as far as possible be unattacked by any solutions or gases with which it comes in contact, so that expenses for repair and replacement and disturbances of the cell due to the diaphragm

[5] EICHRODT, C. W., *Trans. Am. Electrochem. Soc.*, **45**, 390 (1924).

may be reduced to a minimum. The diaphragm should be of as low electrical resistance as possible.

To withstand alkaline liquors, asbestos is often used, in either sheet or woven form. Crude asbestos mineral becomes readily clogged, but asbestos which has been acid-treated and baked or has been subjected to refining manufacturing processes has sufficient mechanical strength so that it may be securely fastened in position without fear of breakage, and is of good porosity so that it does not choke up. Asbestos diaphragms are widely used in chlorine and caustic cells. A modification consisting of a mixture of asbestos, Fe_2O_3, and colloidal ferric hydroxide was employed as a diaphragm material in Townsend chlorine cells, while a mixture of $BaSO_4$ and asbestos wool spread over closely woven asbestos cloth is an effective diaphragm in the Billiter chlorine cell. Portland cement or concrete has been employed in alkaline liquor electrolytes, while woven screens of metal such as nickel or iron with very small apertures, or sheets in which a large number of small holes are punched, are used in certain filter-press type hydrogen-oxygen cells. In the manufacture of electrolytic white lead, heavy linen cloth was the diaphragm material.

For acid electrolytes, linen, muslin, or canvas is employed in nickel refining for the "cathode boxes." Synthetic resinous materials in the form of woven textiles show greater resistance to acid or alkaline electrolytes than do the natural fibers. Examples are the polyamides (Nylon), the polyacrynitriles (Orlon), the vinylidine copolymers (Saran), and those of vinyl chloride (Vinyon). They are finding wider uses, replacing natural textile diaphragm materials. Most clays and porcelains contain too much basic material to be satisfactory, the acid electrolyte combining with the bases in the diaphragm. Fused alumina in plates or manufactured shapes has been employed, as well as "electrofiltros" which consists of fine grains of pure silica crystals cemented together with a small percentage of fused siliceous bonding material. In small-scale work some high-grade porcelains have been used, but their electrical resistance is ordinarily too high for industrial applications. Unglazed porcelain diaphragms were used in the manufacture of para-aminophenol by electrolytic reduction, and are used for chromic acid regeneration. In general, diaphragms are avoided. In some special

cases, as in storage batteries, thin wood sheets serving to pre-
vent shortcircuiting between the plates may be considered as
diaphragms, and retainers such as mats of glass wool may be
considered in the same class.

Tank Materials.   The materials used for tanks for electrolytic
cells are wood, steel, and concrete, with or without linings.   In
the electrolytic refining of metals, the tanks are generally wood
(longleaf pine and in some cases cypress or redwood) or concrete.
Often the cells are lined with lead containing 6 to 8 per cent
antimony to increase the stiffness (the lead weighing 6 to 8 lb
per sq ft), or with mastic or asphalt.   Lead linings cannot be
used for electrolytic solutions containing chlorides.   In some
specialized cases, as in the manufacture of persalts, the tanks
are wood impregnated with paraffin wax.   Practice prefers con-
crete tanks lined with mastic, petroleum pitches, or asphalts in
place of wood.   Considerable attention is paid to the selection
of the proper aggregate so that a dense material may be produced.
The cements employed are of the slow-setting type.

Iron or steel tanks are used for electrolytic cleaners in electro-
plating and for chlorine, caustic, and chlorate cells.   In the case of
chlorine, combinations of steel and concrete are widely employed.
For containers in electroplating, wood serves for the larger tanks
although there has been considerable application of rubber-lined
steel units for universal use.   For small sizes, ceramic ware finds
application.   In silver refining, Thum cells were of ceramic ware,
but there has been a gradual displacement in favor of concrete
cells lined with mastic.   In the Wheeler chlorine cell, composites
of concrete and asphalt serve for parts of the unit.   Minor
applications are made of soapstone for containers, as in small-
scale hypochlorite cells and the covers for the Nelson chlorine
cell.   Mastic concrete (consisting of ground quartz of all sizes
held by a stiff asphaltic material), sulfur-filled concrete, and
carbon-sulfur or carbon-sulfur-sand mixtures have been proposed
and used as acid- and waterproof materials of construction for
cells and cell linings.   For one of the most severe cases of cor-
rosion of materials, that of ferrous and ferric chloride in the
Eustis-Perin process of iron extraction, the tank material was
concrete impregnated with molten sulfur.   Mixtures of these
types are limited to operating practices where temperatures do
not exceed 55 to 65°C.   Small-scale apparatus is sometimes made

with linings of synthetic plastics, while celluloid finds use in the construction of electroplating barrels or drums. Glass is limited to small-scale equipment such as storage batteries.

Rubber-lined tanks are favored in electroplating plants for acid and neutral baths, such as acid pickles, acid zinc and copper solutions, and nickel solutions with both high and low pH.

In the selection and application of the rubber lining, it is important to avoid "rubber compounds" from which organic constituents (derived, for example, from the rubber accelerators) may be extracted by the bath. Such materials may be very harmful in certain bright-nickel plating solutions. The rubber linings are usually applied to steel tanks, either in the form of sheets of rubber (hard or soft) attached by appropriate cements, or are sprayed on to produce seamless coatings. "Stop-offs" are applied especially to insulate portions of plating racks. The ideal material should be adherent, withstand mechanical abrasion, be a good insulator, and resist the action of hot alkaline cleaning baths, acid dips, and the plating baths. The materials include nitrocellulose and other lacquers, usually pigmented; rubber, applied by cementing, spraying, or electrodeposition; and synthetic plastics, including rubber or rubberlike compounds, and various transparent plastics. In many cases flexible tapes are embedded between successive layers, to increase the strength and resistance to chipping.

In the selection of a material of construction for electrolytic cells, a number of factors such as cost, ease of construction, corrosion resistance, life, effect of the material or the lining on the solution, resistance to temperature changes, or attack by warm solutions, availability of the materials, and labor for construction must be taken into account. In the electrolytic refining and electrowinning of metals, perhaps the most widely used construction material is concrete, with either lead or some kind of mastic or asphaltic lining. Special composition concrete tanks painted with asphalt-gilsonite paints have shown long service life. These are cheaper than lead-lined units.

Electrodes for Fused Electrolytes. As anodes in fused-salt electrolytes, in some cases graphite is too expensive, and amorphous-carbon electrodes are more suitable. Such is the case of aluminum where the anode is oxidized to CO and CO_2.

In fused electrolyte cells iron is employed wherever possible.

It is found as the cathode material in magnesium, calcium, and the production of sodium from fused caustic. In a number of important fused electrolyte processes, the only available cathode construction material found to date is carbon, generally rammed in place in the form of a plastic mass of the ground carbon with a binder, the mass afterward being baked. This is the typical construction in an aluminum cell, which consists of a steel pot or box lined with carbon.

Diaphragms and Containers. Diaphragms find little application in fused-salt electrolysis save in the case of the Castner and salt cells for sodium, where wire screens of iron or nickel are employed. The containers are almost universally steel, either bare or lined with ceramic brick or carbon. When the containers are unlined, an effective lining is usually formed by a fused layer of the electrolyte or the material being melted. Examples are found in the preparation of sodium from caustic, the various units for calcium, and the equipment for magnesium. An analogous case is that of fused-alumina furnaces, where the furnace consists of a steel shell protected by a layer of the alumina adjacent to the steel.

Electric-furnace Electrodes. Amorphous-carbon and graphite electrodes enter into the manufacture of electric steel, ferroalloys, CaC_2, cyanamide, SiC, fused alumina, graphite; aluminum, magnesium, calcium, and sodium metals; phosphorus, H_3PO_4, and CS_2; chlorine, caustic soda, chlorates; electric-furnace melting of nonferrous alloys; primary cells; as well as other minor applications. From the viewpoint of the raw materials used, the methods of manufacture, and their applications, the electrodes may be subdivided into amorphous-carbon electric-furnace electrodes, amorphous-carbon electrodes for aluminum, graphite furnace electrodes, and graphite shapes for electrolytic work.

Electrodes for electrothermic work serve as the refractory conductors of the electric current and do not enter into the reactions taking place in the furnace or other apparatus in which they are used. In many cases the impurities of the electrode either do not get into the product of the furnace or, if they do, make no appreciable difference. Thus a satisfactory electrode for electrothermic purposes may have an appreciable ash content and show a comparatively high resistivity. The raw materials

are low-ash anthracite, which after calcination is ground so that a high-strength aggregate may be obtained.

Electrodes for fused-salt electrolysis, such as the production of aluminum, must be low in impurities in that these are transmitted to the metal produced in the furnace. The raw material for these is petroleum coke, a pure low-ash by-product of petroleum oil refining. The purity and resistivity of the electrodes (anodes) are important, because of the low voltages at which the furnaces operate.

Graphite electrodes are made from either low-ash coals or petroleum coke, common practice being first to form the amorphous electrode which is later graphitized. Artificial-graphite electrodes are with few exceptions formed by extrusion. Amorphous-carbon electrodes for electric-furnace work are made by both molding and extrusion methods. In the case of aluminum electrodes, molding is replacing the extrusion operations formerly employed. A typical manufacturing flow sheet for electrodes[6] is shown in Fig. 265. The carbonaceous materials are crushed and calcined to remove volatile matter in either gas-fired or electric equipment. The calcined material is ground and pulverized to a particle size or range of sizes particularly adapted to the type of electrode being made. In the case of large electrothermal electrodes, the aggregate will contain a considerable amount of coarse particles. In some plants the ground materials are screened and the various-sized products mixed in the desired proportion. The dusts are mixed with tar or pitch binders and shaped by either molding or extrusion to produce "green" electrodes. These are baked in either gas-fired or electrically heated furnaces, being held in place by ground calcined carbonaceous material termed "packing." After baking, the electrodes are cleaned and either used as such or machined for specific uses.

Individual electrothermal electrodes are made in many sizes. A typical one 20 in. in diameter, 180 in. long, weighing 3,180 lb, is shown in Fig. 266. They are made as large as 48 in. in diameter. For continuous feed, both ends are drilled and tapped so that a small threaded plug or dowel pin of electrode material may be screwed into the end of one electrode and the adjacent

[6] MANTELL, C. L., "Industrial Carbon," 2d ed., p. 268, D. Van Nostrand Company, Inc., New York, 1946.
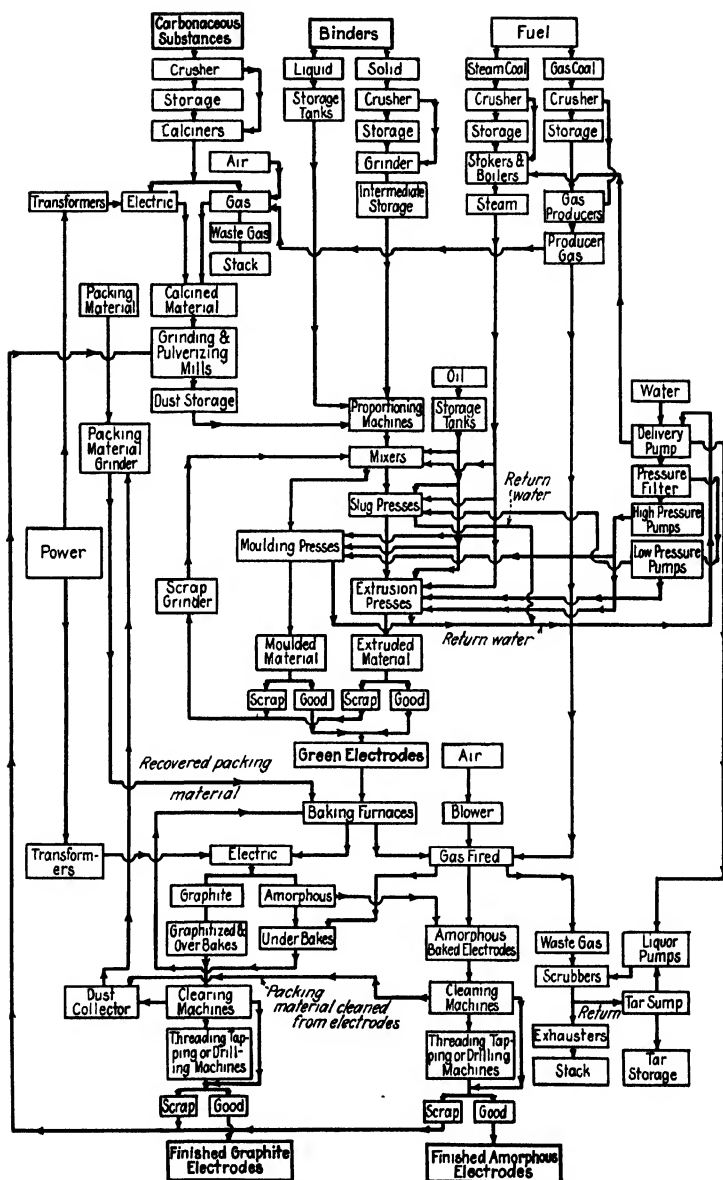
FIG. 265. Flow sheet of carbon-electrode manufacture.

end of the next one. Such an operation is shown in Fig. 267. A size finding considerable employment in carbide furnaces is 20 by 20 in. square, a number of which are connected or joined together in bundles.
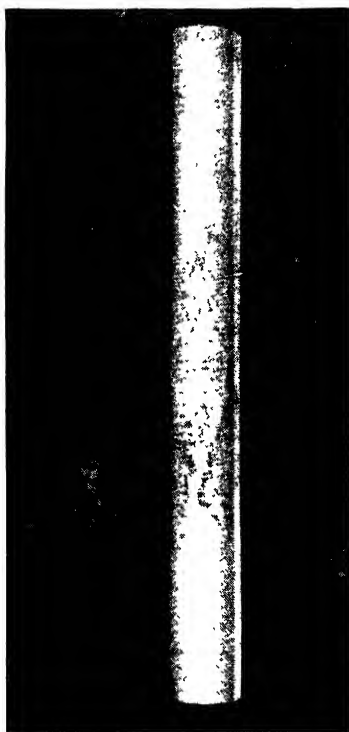
Fig. 266. A 20-in. carbon electrode, 20 in. in diameter by 180 in. long. (*National Carbon Company*.)

Fig. 267. Joining electrodes. (*National Carbon Company*.)

Continuous Electrodes. There has been developed within recent years a self-baking electrode formed continuously from a soft carbon mixture which is baked in the same furnace in which it is used. It thus provides a continuous electrode. The first electrode of this kind was built by Söderberg in 1909. The Söderberg electrode consists of a ribbed cylinder of thin sheet iron into which the electrode paste is filled. The electrode is added to from time to time by lengthening the cylinder and filling up with fresh paste. The paste for the electrode is the

same and made in the same manner as for ordinary electrodes. The lower end of the electrode is baked by waste heat from the furnace. In use, the electrode consists of a baked and an unbaked part. The baking of the electrode takes place as it is allowed to slip through the holder. The holder is of the water-cooled clasp type. The slipping is effected by loosening the grip of the holder until the electrode slides by its own weight.

Fig. 268. Commercial setup for measuring resistivity of a large electrode (*Acheson Graphite Company.*)

This manipulation of the electrode may also be effected from a place situated at some distance from the furnace. Slipping of the electrode is carried on under full load. The current is maintained during slipping by means of a sliding contact between the holder and the electrode casing.

Electric-furnace Shells and Linings. In electric-furnace work the container of the furnace is always sheet steel or cast iron, refractory lined, the type of refractory used depending upon the furnace operations. The refractory may be acid, such as silica in the form of silica brick or ground material mixed with a binder and tamped into place; or basic, when it is either magnesite, dolomite, or in some cases chromite. Various other refractories

may be used, such as those of the clay type or the aluminous refractories and in special cases SiC materials. For preventing large heat losses, insulators may be of aid, but they are never exposed to the furnace bath. They are fireclay, diatomaceous earth, kieselguhr, magnesia, asbestos compositions, or other special products. In cases where other materials fail as the result of high temperatures, the temperatures exceeding the point where the refractory gives satisfactory load service or else the melting point of the refractory being exceeded and reducing conditions maintained in the furnace, carbon refractories find application. They are in the form of preshaped blocks or they may be rammed in place. For the base of electrical resistance furnaces, particularly of the graphite, SiC, and electrode-baking furnaces, ground-brick grog or gannister is employed. The side walls and heads of such furnaces are built of high-quality, clay-refractory brick. For insulating materials in such furnaces the usual substances cannot be employed, in that they would contaminate the charge of the furnace. Insulation is therefore obtained by the use of relatively thick layers of finely ground carbonaceous materials such as those made from petroleum coke or low-ash anthracite, calcined before use.

Furnace linings have as their function the holding of the charge and the retaining of the heat in the furnace, preventing its loss. Desirable furnace-lining properties are (1) high melting point, (2) resistance to abrasion, (3) mechanical strength both at ordinary and at the operating temperatures of the furnace, (4) low coefficient of expansion, (5) low thermal conductance, and (6) resistance to disintegration as the result of sudden temperature changes and slagging action. The term "refractory" includes all these properties. No one material has them all to as high degree as desired. For example, high melting point is usually associated with relatively high thermal conductivity. Refractories of low electrical conductivity are usually desirable for furnace walls and roofs. Some of the less common types of steel furnaces depend upon having a refractory at the bottom which is a good electrical conductor.

Carbon has the highest melting point (about 3500°C) of the possible materials useful as refractories, but it is limited to reducing atmospheres. It is a good thermal and electrical conductor. Zirconium oxide, having a melting point above 2600°,

is chemically inert, withstanding the action of fused alkalies and fused silica. It has a low coefficient of expansion (8.4×10^{-7}) and a high electrical and thermal resistance. It has the disadvantage of being relatively expensive. Magnesite in the form of pure magnesia has a melting point of 2800°C, but the impure magnesite of commerce melts at about 2160°.[7] The porosity of magnesite refractories is fairly high, being 25 to 30 per cent. The density of dead burnt magnesite is about 3.5, that of fused MgO 3.58. The bulk specific gravity of brick is 2.6 to 2.75. Bleininger states that magnesite bricks do not resist sudden temperature changes well and show a decided tendency to spall under such conditions. This type of refractories in contact with clay is attacked vigorously by the latter at furnace temperatures. Silica materials attack it likewise, although less violently. Carbon also reacts with magnesia at high temperatures, as does phosphorus.

Highly burnt impure dolomites are a cheaper refractory which replace magnesite but do not equal it in its refractory qualities. Silicon carbide in its crystalline form dissociates at about 2240°C. It does not fuse or soften below this point but under oxidizing conditions decomposes to a considerable extent. Silicon carbide refractories are useful for their high thermal conductivity, their low coefficient of expansion, rigidity and mechanical strength. The porosity of SiC products varies between 15 and 20 per cent, and the bulk specific gravity is from 2.1 to 2.5. It resists load conditions at furnace temperatures (1400 to 1450°C) without any appreciable deformation. It is made in bricks through the inter-locking of crystals as the result of refiring in electric furnaces, or by the use of bonding materials. It is a reducing agent for metallic oxides at high temperatures. It is decomposed by iron and its slags and by lead oxides. It is attacked by Na_2CO_3 and alkali sulfates or hydrates, by sodium silicate at 1300°, slightly by MgO at 1800°, and by fused borax or fused cryolite. Silicon carbide "veneer" bricks are made consisting of a layer of SiC on high-grade clay refractories.

Because of its high fusion point, 2050°C, alumina is inherently an excellent refractory. It has the disadvantage of showing a large contraction upon heating. A similar situation exists in the case of the aluminum ore, bauxite, which must be com-

[7] KANOLT, C. W., *Natl. Bur. Standards (U.S.) Technol. Paper* 10.

pletely calcined before it can be used for furnace linings. Fused alumina brick has shown much longer life on furnace roofs than silica brick, when not exposed to lime vapors such as occur on a basic steel furnace slag. As the silica content of alumina mixtures increases, the fusion point decreases until a compound of the composition $Al_2O_3 \cdot SiO_2$ is formed, melting at a temperature of 1816°C and corresponding in composition to the mineral sillimanite. The melting point of bricks made from a bauxite-clay mixture corresponding to sillimanite composition melts at about 1790°C.[8] Spinel, $MgO \cdot Al_2O_3$, melts at about 2130°C. In certain sections of electric furnaces, bricks of this material give better service than magnesia or magnesite.

Silica exists either as quartz melting below 1470°, crystobalite melting at 1625°, or tridymite. Three kinds of silica brick are made. The first is of high silica content (96 per cent) with lime as a binder; the second is of lower silica content with clay as a binding material; and the third is a natural brick molded direct from natural rock of mixed quartzite. Silica bricks withstand load conditions satisfactorily, even at temperatures up to 1500°C under a pressure of 50 lb per sq in. As a whole, their resistance to slagging action is not great because of their high porosity and acid character. They show a greater tendency to crack or spall upon chilling or rapid heating than do clay refractories. The clay-bonded silica brick are less refractory than those which are lime bonded. The high-silica-content brick expand considerably on heating, due to the inversion point of quartz at 575°C which is accompanied by a volume increase. They are good heat insulators and are used for electric-furnace roofs.

Chromite bricks are made from chrome-iron ore containing 38 to 40 per cent Cr_2O_3 or better. They have a melting point of about 2180°C and are difficult to sinter. Chromite refractories are employed in furnaces as partings or separation layers between silica and magnesite bricks. They are considered neutral as regards chemical reactions. They are excellent conductors of heat and show a fairly high coefficient of thermal expansion.

The purest type of clay is that represented by carefully washed kaolin, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, melting at 1750°. The clays from

[8] *Ibid.*

which brick are made may be subdivided into flint clays corresponding in composition to the best grades of kaolin, siliceous clays showing a higher content of silica than kaolin, and plastic clays. The melting point of flint-clay refractories may be taken as between 1600 and 1680°C, of siliceous clay brick 1580 to 1630°, and of plastic clays 1500 to 1600° in the case of first-grade refractories.

The most important electric-furnace linings from the viewpoint of all-round utility and cheapness are those of silica, dolomite, magnesite (either as brick or as material rammed in place), and carbon. The last may be put into the furnace bottom either in paste form, in which case it is in a plastic condition and may be made to conform to the furnace shell, or as preshaped blocks. These may be of either amorphous carbon or graphite.

Conductors and Busbars. Electrochemical plants require heavy busbar equipment. A busbar, as the term is usually applied, means an electrical conductor arranged to receive the current from one or more incoming circuits and to deliver it to one or more outgoing circuits. Busbars at centers of distribution, such as powerhouses and substations, serve to facilitate switching of the current from one source of supply to another and to change the amount supplied to any particular circuit or load point. Electrolytic plants probably represent the largest concentrated current loads in existence.

Hard-drawn copper and hard-drawn aluminum are the usual materials for busbars. The electrical properties of these two materials are given in Table 95. In America aluminum has been used more extensively for high-tension transmission lines than for busbars, but in England and some European countries the reverse is true.

The object of any electrical conductor is to transmit current with the smallest loss economically possible, and since the loss in the conductor is proportional to its length, the current density in short-length busbars may usually be higher than in long transmission lines. The limiting condition in a transmission line is the voltage drop or energy loss; in a busbar it is usually the temperature rise. However, since economical conditions always involve a balance between an investment to prevent loss and the value of the power saved, it may well be, in the case of large stations involving a heavy current value, that the energy loss in

TABLE 95. PROPERTIES OF BUSBARS

Characteristic	Copper, hard	Aluminum, hard
Conductivity at 20°C	99 %[1,2]	60 97 %[1]
Resistivity at 20°C	1 742 microhms/cm^{3}	2 828 microhms/cm^{3}
Resistance-temperature coefficient at 20°C	0 00393/°C	0 00403/°C
Density at 20°C . . .	8 89 g/cm^{3}	2 703 g/cm^{3}
Length-temperature coefficient at 20°C . .	0 0000167/°C	0 000023/°C
Change in resistivity with change in temperature[3]	0 0070 microhm/ cm[3]/°C	0 0115 microhm/ cm[3]/°C

[1] International Annealed Copper Standard.

[2] While a conductivity of 97 per cent of the Intern tional Annealed Copper Standard is generally used for hard-drawn copper wires of comparatively small cross section, it is common practice to assume as high as 99 per cent conductivity for hard-drawn copper busbars.

[3] The value for the change in resistivity with change in temperature is the sum of the resistance-temperature coefficient and the length-tempera' ire coefficient, multiplied by the resistivity at 20°C.

the busbars may be limited by the voltage drop rather than the temperature rise.

The voltage drop in any conductor is directly proportional to its length, directly proportional to its resistance, inversely proportional to its conductivity, and inversely proportional to its cross section. Therefore, if we consider two conductor bars, one of hard-drawn copper and the other of hard-drawn aluminum, each of exactly the same length, shape, and cross-section area, then, with the same current flowing in each, the voltage drop in the aluminum will be greater than the drop in the copper in the proportion that the conductivity of copper bears to that of aluminum, *viz.*, 99.00/60.97 = 1.6237. Assuming aluminum and copper bars having cross sections of the same area and shape, the voltage drop in the aluminum will be 62.37 per cent greater than that in the copper bar for the same current.

The temperature rise of a conductor is proportional to the energy loss, and this is equal to the square of the current multiplied by the resistance. In two bars, one of aluminum and the other of copper, of the same length and cross section and for the same temperature rise, the current will have the following proportions:

$$\frac{I^2(\text{Al})}{I^2(\text{Cu})} = \frac{60.97}{99.00} \qquad \frac{I(\text{Al})}{I(\text{Cu})} = \sqrt{\frac{60.97}{99.00}} = 0.78477$$

On this basis, the area of an aluminum bar to give the same temperature rise as a copper bar with the same current should be approximately 27.4 per cent greater than that of the copper. However, since the temperature of a conductor is dependent not only upon the rate of energy expended but also upon the rate of dissipation of heat from its surface, the above ratio is too large.

For a temperature rise of 30°C above an air temperature not exceeding 40°C, the following formula gives the current-carrying capacities for single aluminum and copper flat bars and round rods (hard drawn). This formula is based on bars painted with a dull black paint of high heat emissivity. For brightly planished bars these values of current should be reduced from 20 to 25 per cent.

The general formula for flat bars (long axis vertical) and round rod is

$$I = p^{0.43} \sqrt{a} \times 27.0 \sqrt{\frac{E^{5_4}}{(1 + tE)r}}$$

where p is the perimeter of bar in centimeters, a is the cross-section area in square centimeters, r is the resistivity of the metal in microhms per centimeter cube at temperature of the surrounding air, t is the resistance-temperature coefficient of the metal, I is the current in amperes after stable conditions have been attained, and E is the temperature excess of the surface of the metal above that of surrounding air. By substituting the values of r at 40°C, and the values of t and E, the following formulae are obtained:

Flat Bars	Round Rods
For Al, $I = 122.39p^{0.43}\sqrt{a}$	For Al, $I = 210.9a^{0.715}$
For Cu, $I = 152.53p^{0.43}\sqrt{a}$	For Cu, $I = 262.8a^{0.715}$

From the application of these formulae it results that, for flat bars of the same width, the aluminum bar has approximately 33 per cent greater thickness than the copper. For round bars the aluminum bar is 7 per cent greater in diameter than the copper bar. Since the area of a rectangular aluminum bar is approximately one-third greater than a copper bar for the same temperature rise, it therefore weighs only 41 per cent of the copper bar.

Ordinarily, the economics markedly favor aluminum as busbar material for high amperage loads and cell distribution systems.

POWER GENERATION AND ECONOMICS

From the electrical viewpoint, the power load for electrochemical processes is almost an ideal one, in that it is ordinarily continuous 24 hr of the day and every day in the year. In electrolytic work the voltage per unit tank or cell is low; for example, copper refining, multiple system 0.2 to 0.4 volt per tank, nickel refining 2.4 to 2.5, electrowinning of copper 1.9 to 2.4 and of zinc 3.5 to 3.7, chlorine 4.1 to 4.3, aluminum 5.5 to 7, magnesium 6 to 9. The amperage is relatively high. Small chlorine cells may be only 1,000 amp, but large ones from 10,000 to 25,000 amp; small aluminum cells may be 14,000 amp, but large ones as high as 50,000, while magnesium units are of the same order. A sufficient number of units are connected in series in order that machines of standard voltages may be employed. Such a situation is commonly found in electrorefining and electrowinning of metals, the electrolysis of salt solutions for the production of chlorine and caustic, and the manufacture of metals such as aluminum, magnesium, and sodium from fused salts.

The total power requirements of electroprocess industries in the United States show a tendency to increase at a rate somewhat more rapid than those of industry as a whole. From 1929 through 1943, the total annual power requirements of national manufactures increased about two times—from 71 to 147 billion kilowatthours. For the same period the total annual requirements of national electroprocess industries increased almost four times—from slightly over 9 billion to almost 38 billion kilowatthours (Figs. 269 and 270).

The power requirements of electric-furnace alloys have grown. In 1936 these requirements were of the order of 1.75 billion kilowatthours. In 1943 they had increased about three times.

In copper and zinc, electrothermal and electrolytic reduction power requirements have continued to climb. At least as far as zinc is concerned, the depletion of ores which may be treated by

717

pyrometallurgical methods makes it imperative that the industry utilize electrowinning procedures to treat the complex lead-zinc ores not amenable to pyrometallurgy. This places a premium on electroprocess methods. The steady upward trend in power consumption in these two industries is marked. From about $\frac{1}{2}$ to $1\frac{1}{2}$ billion kilowatthours per year during the period 1926 to
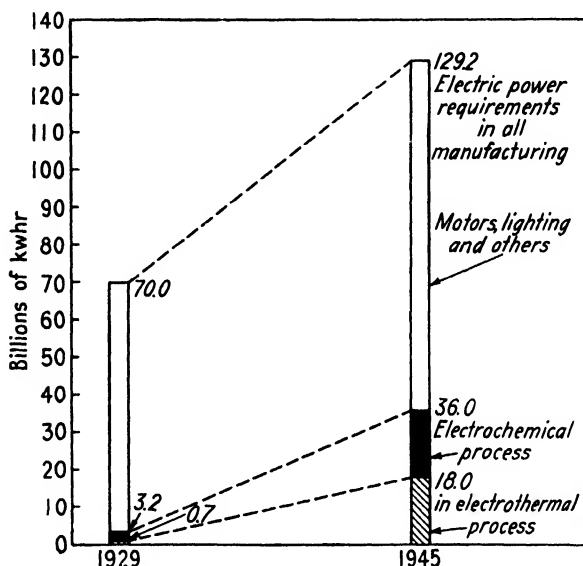
FIG. 269. Electric power requirements in all manufacturing, electrochemical processes, and electrothermal processes in the United States in 1929 and 1945. (SOURCE: *Federal Power Commission.*)

1939, these requirements reached almost 3 billion kilowatthours in 1943.

For calcium carbide, chlorine and caustic, electrothermal steel, and other electroprocess industries, there was a steady rise of power consumption prior to the Second World War, rapid expansion during the war, and continued rise since. These are more or less standard products to which must be added numerous other products of the electric furnace and electrolytic cell, such as metallic calcium, lithium, sodium, phosphorus and electric-furnace fertilizer, electrolytic iron, chromium and manganese, as well as chlorates and perchlorates.

It appears that electroprocess industries will continue to grow
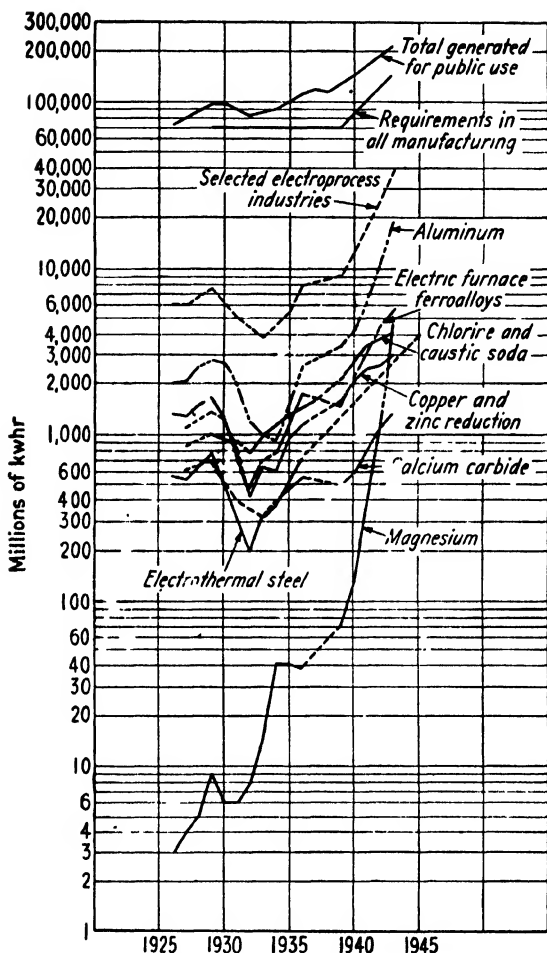
FIG. 270. Electric power generated for public use and power requirements in all manufacturing and selected electroprocess industries, 1926–1943, in the United States. (SOURCE: *Federal Power Commission.*)

at an accelerated rate. One factor relates to the exhaustion of many high-grade raw materials and the need for using what hitherto has been left in the ground or in the tailings pile. The value of the electrolytic cell and the electric furnace in the production of high-grade industrial materials from low-grade and complex ores is recognized. In effect, electroprocess industries

more frequently than heretofore offer a means for meeting the continually increasing demands of manufacturing industry for high-quality materials of controlled specifications.

On the other hand, the very nature of electroprocess industry, in which power is a basic ingredient and a raw material, demands low unit price for large homogeneous blocks of power, supplied uninterruptedly. These requirements vary with each industry. An aluminum plant must have blocks of at least 20,000 to 35,000 kw for each production unit. The power supply must be continuous; it cannot be shut off at will without expensive restarting of operations. Inasmuch as 8 to 10 kwhr are required per pound of aluminum, the cost in mills, not cents, cannot be much more than 2 to 3.5 mills per kilowatthour, depending upon location. Even at 2 mills per kilowatthour, this power requirement represents between 20 and 25 per cent of the production cost of the metal.

The major existing and potential locations for electroprocess industries in the United States and Canada have been hydro centers. In the East, Niagara Falls with the surrounding territory in the United States and Canada has been a traditional center for this type of industry. The Tennessee Valley with its surrounding area has become another important center since the building of the power facilities of the TVA. There are other rather isolated centers of major electroprocess industries.

Already in the Pacific Northwest, Bonneville and Grand Coulee dams, over a high-capacity transmission network covering most of Washington and Oregon, furnish more than half of all the power consumed in the region. However, the development at these two dams is a small portion of 25,000,000 kw estimated to represent the ultimate potential of the Columbia River and its tributaries in the United States. By 1952 another 1,500,000 kw are expected to be installed at Grand Coulee and several other dams.

The Colorado River dams, particularly the Colorado-Big Thompson, Parker-Boulder, Bridge Canyon-Glenn Canyon projects, will increase the availability of firm, low-priced blocks of power in Southern California and in the Colorado-Utah-Salt Lake basin by means of a system of high-capacity transmission lines. These and other projects will add more than 1,000,000 kw of capacity to the areas involved.

Canada, particularly the Eastern provinces, has some 10 million of its potential 50 million horsepower already installed at a number of dams. Most of the development has taken place in the Province of Quebec. Hydro development of the Saguenay has brought Arvida into being as a focal point of electrolytic and electrothermal plants. The Shawinigan Water and Power Company has hydro installations on the St. Maurice River (one of the largest tributaries of the St. Lawrence River) for a total of well over a million horsepower. Shawinigan Falls is an electrochemical industries center. Another five development sites of the same river which are projected for construction would add another million horsepower. These hydro plants are interconnected by a wide transmission network. On the average, firm power in the vicinity of 3 mills per kilowatthour can be obtained from these developments.

In Ontario, the Ontario Hydro Commission has tapped about a third of the total potential development of the Province, estimated at some 9 million kilowatts.

Direct-current Power Generation. It is estimated that over 200,000-kw capacity represents the annual peacetime purchase of d.c. machines for electrolytic service. Direct-current power can be obtained in several ways:

I. Purchased alternating current converted to direct current by:
    A. Synchronous converters
    B. Motor-generator sets
    C. Rectifiers
        1. High-voltage, mercury arc
        2. Low-voltage, copper oxide and selenium
II. Generated power:
    A. A.c. generation and conversion as for purchased power
    B. D.c. generation
        1. Geared steam turbines
        2. Steam engines
        3. Diesel engines
        4. Hydro stations

The bulk of d.c. power is obtained from synchronous converters or motor-generator sets, although a few geared steam turbines are in operation.

In 1929 a Canadian company made the first large installation of mercury-arc rectifiers for electrochemical work. The equipment was rated 16,800 kw at 560 volts. The use of mercury-arc

rectifiers for this work has been successful and has tended to replace rotating machines for these applications.

Mercury-arc rectifiers are used in the electrolytic production of chlorine, hydrogen, hydrogen peroxide, aluminum, zinc, and other metals. Because the transformers, and in some cases the a.c. switchgear which represents a large proportion of the total

Fig. 271. A 55,000-kva rectifier at the Alcoa works of the Aluminum Company of America. (*Chemical Industries.*)

rectifier equipment, may be installed outdoors, building costs, foundation expense, etc., are materially reduced as compared with those necessary for other forms of conversion equipment. There are no continuously moving, heavy current-carrying parts; hence, maintenance on rectifiers is low, particularly in the presence of corrosive atmospheres.

Switchgear equipment and control systems for use with rectifiers have been developed and are adapted to meet various operating conditions. The installations made have been justified on the basis of installed first cost and decreased operating expense. Most of the installations have consisted of the so-called "multianode" tanks operating in the 500- to 800-volt range. Figure 271

shows a 55,000-kva installation at the Alcoa works of the Aluminum Company of America supplying power for alumina reduction.

The introduction of the ignitron-type rectifier, shown in Fig. 272, extended the use of mercury-arc rectifiers in the medium-voltage range because of its improved efficiency as compared with that of the multianode rectifier. The ignitron-

Fɪɢ 272.   Ignitron-type rectifier.   (*General Electric Company.*)

type rectifier has been used for several years in the mining and transportation fields.

Levy[1] states that, at 1,500 kw and full-load capacity, the over-all efficiencies of the converter, motor-generator set, and rectifier are as follows:

Volts	Shunt converter	M.-G. set	Rectifier
250	92.3	89.9	90
600	93.5	90.3	94.3

[1] Lᴇᴠʏ, C. C., *Chem. & Met. Eng.*, **43,** 658 (1936).
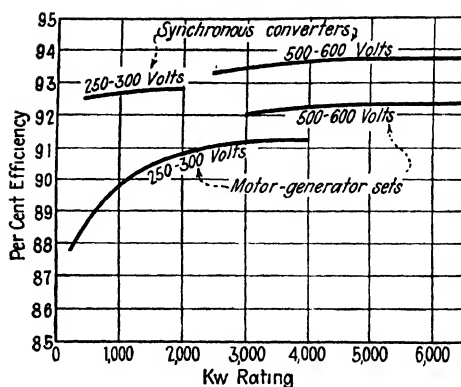
FIG. 273. Efficiency of synchronous converters and motor-generator sets.
Converter efficiency includes losses of transformer and induction regulator or booster and 0.3 per cent a.c. lead loss. Motor-generator set efficiency is based on 100 per cent power factor for motors. All losses are calculated or measured in accordance with the AIEE rules. The resulting efficiencies are close to the actual efficiencies.
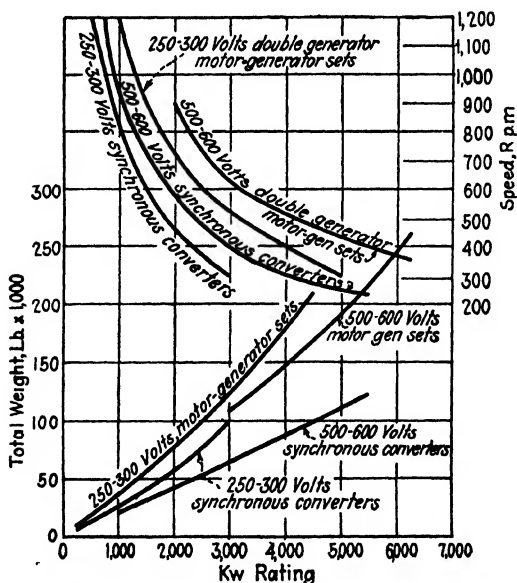
FIG. 274. Speed of synchronous converters and motor-generator sets.

Requirements of the electrolytic circuits are usually definitely known.   As a rule a voltage range of 10 per cent plus and minus will be ample to meet all operating requirements.   This range is easily obtained on the ordinary self-excited generator.

A comparison of a.c. generation followed by conversion to direct current, and d.c. generation, shows that the latter has the advantages of lower first cost, slightly lower fuel cost, lower labor

Fig. 275.   Synchronous converters in aluminum production; 2,500 kva, 500 volts, six phase, 60 cycles, 400 rpm.   (*Chemical Engineering*.)

cost, with a possibility of lower maintenance cost, but the disadvantage of lack of flexibility when interconnected with other power systems, or in the conversion of the plant to other than electrolytic use, or when major changes are made in electrolytic circuits.

In general, synchronous converters show higher efficiencies than do motor-generator sets.   This relation is shown in Fig. 273. Speeds of the different types of machines are given in Fig. 274. In general, synchronous converters cost more than do motor-

generator sets.   Some typical power plants are shown in Figs.
275, 276, and 277.

Rectifiers.   Selenium rectifiers with normal plate spacing and
normal convection cooling are 65 to 85 per cent efficient, depend-
ing upon the circuit arrangement.   This efficiency is maintained
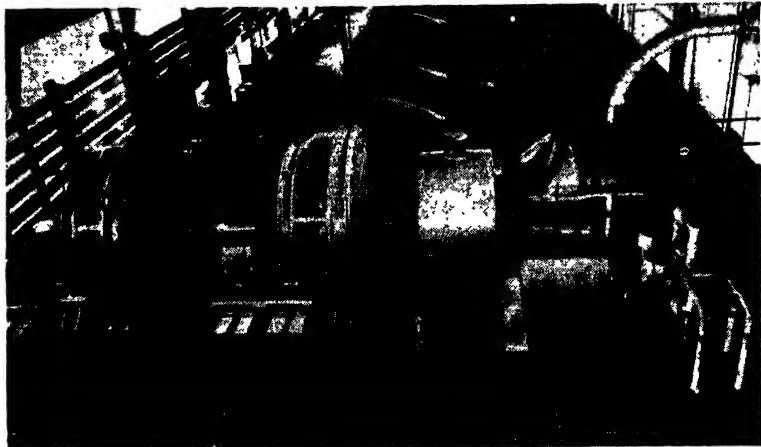
Fig. 276.   Geared turbine d.c. generators in copper refining; 2,800-kw, 125-
volt, two 11,200-amp generators.   (*Westinghouse Electric and Manufacturing
Company.*)
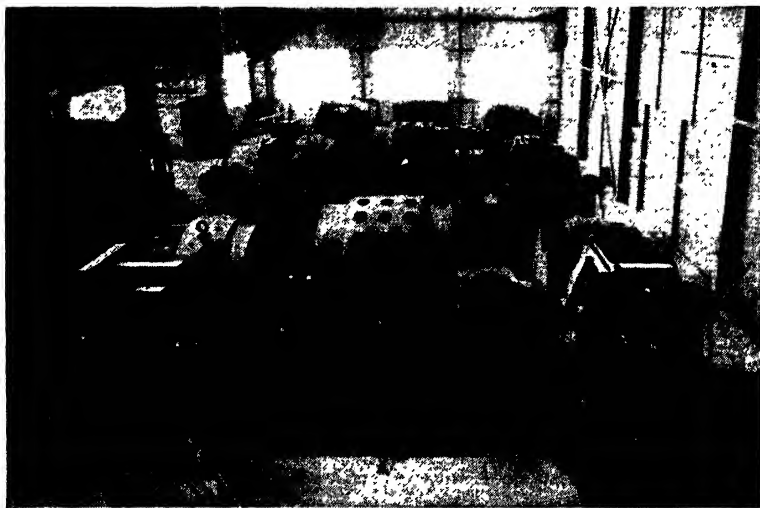
Fig. 277.   Motor-generator sets in electrolytic service; 3,840-kw, 320-volt
generators with 6,600-volt, 25-cycle, three-phase, 500-rpm motors.

approximately from 20 to 150 per cent of full load. Most electrical apparatus attains maximum efficiency only in the region of full load.

Rectifier efficiencies are calculated in two ways: (1) as ratio of output to input when both are measured with a wattmeter, or (2) as ratio of output to input when the output is measured with a voltmeter and an ammeter of the moving coil type.
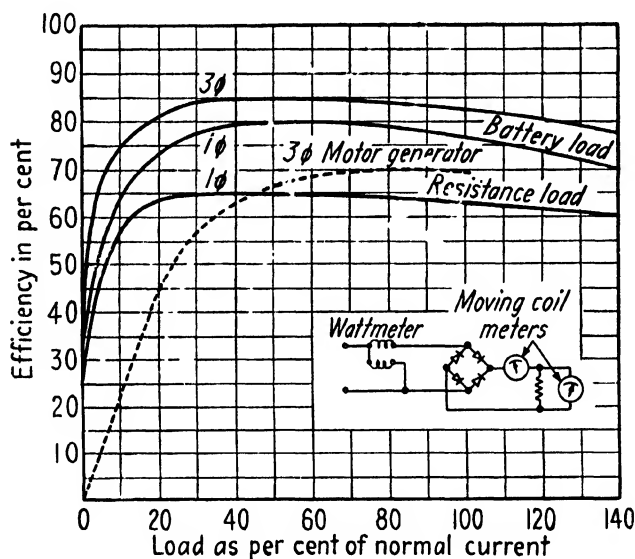
Fig. 278. Efficiency of selenium rectifier operating at full-load voltage, compared to average typical efficiency of a motor-generator set with exciters. (*Federal Telephone & Radio Corp.*)

The measure of efficiency derived by the first method, usually called the "watt efficiency," is about 85 per cent at full load. This figure is independent of plate size since the per-plate current ratings are such that the same final plate temperature is reached by the rectifier in any case. It is also independent of the type of load and rectifier circuit arrangement.

Volt-ampere efficiency, on the other hand, depends upon the output voltage and current form factors. These vary considerably with types of loads and rectifier circuit arrangements. Figure 278 shows typical efficiencies for various load conditions.

Rhea and Connell[2] described rectification and power supply for the electrolytic industries.

During the war years from 1939 through 1945, the electrolytic industry was very greatly expanded. In the aluminum, magnesium, chlorine, copper, and zinc industries the amount of conversion equipment was expanded from approximately 1,500,000 to approximately 4,500,000 kw for both Canada and the United States. At the peak of operation during the war, these five electrolytic processes consumed approximately 31 billion kilowatthours of energy annually. This is more energy than is consumed by any other single industry.

Table 96 gives a summary of the amount of conversion equipment installed in these five industries in the United States and Canada. Of the total of approximately 4,500,000 kw of conversion apparatus, approximately 3,500,000 kw is in mercury-arc rectifiers.

TABLE 96. SUMMARY OF CONVERSION EQUIPMENT IN UNITED STATES AND CANADA

	Rotating machines, d.c. kw	Static rectifier, d.c. kw	Total d.c. kw
Aluminum	516,985	2,941,750	3,458,735
Magnesium. . .	72,800	448,140	520,940
Chlorine.......	114,370	173,790	288,160
Zinc . .	169,100	58,736	227,836
Copper.......	55,230	0	55,230
Total. .	928,485	3,622,416	4,550,901

Nearly all the conversion equipment installed in aluminum reduction plants since 1931 has been of the mercury-arc rectifier type. The only complete and new installation of rotating apparatus covers gas-engine-driven d.c. generators installed during the war because of a shortage of power. They were installed in a location where natural gas was plentiful.

Amperages per line are from 20,000, 26,500, 32,000, and 50,000 to 60,000. The 60,000-amp installed equipment supplies cell lines that may be considered to have a rating of

[2] RHEA, T. R., and CONNELL, B. R., *Trans. Electrochem. Soc.*, **90**, 175–196 (1936).

50,000 amp nominally; therefore, these lines have some installed spare capacity.

Line voltages are of the order of 525 to 645, 500 to 700, and 0 to 640 for Söderberg type cells, started at low voltages.

Generally there are two rectifier units supplied from one rectifier transformer. For example, a rectifier unit is a complete assembly with its own heat exchanger, firing circuit, and vacuum system. The most common rating of a unit is for the 5,000-amp, 12-anode ignitron.

Of the approximately 525,000 kw of conversion apparatus installed in magnesium-producing plants, 75,000 kw are in rotating apparatus and the remainder in mercury-arc rectifiers. Most of the conversion apparatus was installed during the Second World War.

Amperages per line are 20,000, 30,000, and 60,000. Line voltages are 80 to 600, 0 to 365, and 220 to 600.

There are so many different kinds of chlorine cell lines that it is difficult to compile very complete data on them. About every type of conversion equipment is represented and many operating voltage levels. Approximately 175,000 kw of conversion equipment is in mercury-arc rectifiers and 115,000 kw in rotating apparatus.

Typical chlorine cell lines use from 7,500 to 10,000 amp and in the later installations at 750 volts to obtain the higher conversion efficiencies. Some cells are designed for 1,800 to 2,000 amp, and a number of such cell lines are supplied from a common d.c. bus.

Zinc and copper cell lines usually require about 10,000 amp. Zinc cell lines have usually been installed at 500 to 600 volts, while copper cell lines have been installed at 200 to 300 volts. Some foreign installations have been made using voltages up to 800 or 850 volts.

For normal operation, the cell line is operated at substantially constant d.c. voltage. Where rectifiers are applied to zinc lines, the voltage adjustment has been obtained by regulating transformers or grid control. There have been no rectifiers applied, in the United States, to copper processes, probably because of the low d.c. voltage requirements and because of the state of the art at the early dates at which most of the copper lines were installed.

Figure 279 shows the cell-line characteristics for zinc as well as aluminum, magnesium, and chlorine. The cell-line characteristics of zinc and copper are nearly alike.

Many factors of design are involved in providing the heavy amperage currents for electrolytic industries.[3]
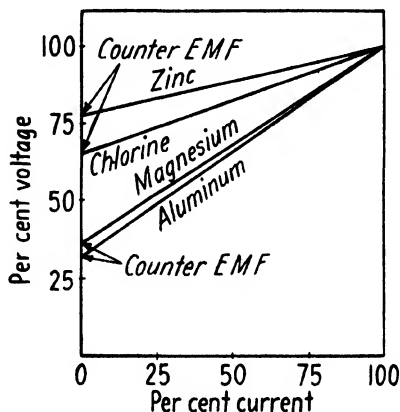
FIG. 279. Cell-line volt-ampere characteristics for aluminum, magnesium, chlorine, and zinc.

Alternating-current Power. Electric-furnace products and electric steel are made by the use of a.c. power. The furnaces involve the use ordinarily of multitap transformers with regula-

[3] HOUSLEY, J. ELMER, and WINOGRAD, H., Alcoa Rectifier Installation, *Trans. Am. Inst. Elec. Engrs.*, **60**, 1266 (1941); MARTI, O. K., and TAYLOR, T. A., Wave Shape of 30- and 60-phase Rectifier Groups, *Trans. Am. Inst. Elec. Engrs.*, **59**, 218 (1940); BOHN, D. I., and GUTZWILLER, W. E., Rectifiers Adopted for American Aluminum, *Elec. World*, **110**, 1585 (1938); KAESTLE, F. L., Rectifier Equipment in the Electrochemical Field, *Trans. Electrochem. Soc.*, **76**, 453 (1939); "Rectifier Wave Shape," Edison Electric Institute, April, 1937; Heavy Current Mutators for Electrolysis, Arvida, Canada, *Brown Boveri Rev.*, October, 1940; RHEA, T. R., Wide Range D.C. Voltage Adjustment in Large Mercury-arc Rectifiers, *Gen. Elec. Rev.*, **44**, 611 (1941); MERTENS, F., "The 26,000-kw. Rectifier Installation of the Zinc Plant at Magdeburg," Brown Boveri Cie., Nachrichten, January–March, 1935; MERTENS, F., "A Rectifier Installation for 80,000 Amperes at 800 Volts for Operation of Electrolytic Process," Brown Boveri Cie., Nachrichten, January–March, 1940; RIMLINGER, L. J., Arc Rectifiers Succeed in Chlorine Production, *Elec. World*, **109**, 411 (1938); BUNET, PAUL, The Engineering Development of Electrochemistry and Electrometallurgy, *Elec. Eng.*, **54**,

tors, controls, instruments, switches, and auxiliary equipment. The electric circuits show very high amperage values at moderate voltages. For steel furnaces, transformers are usually special, while for other purposes, other than large sizes, they ordinarily involve no unusual features of design.

In contradistinction to electrolytic work where the units are connected in series because of the low voltage per tank or cell, in electrothermal work there is a separate electrical circuit for each furnace. Furnace voltages are in the range of 50 to perhaps 250 volts. When the equipment is intermittently operated, a number of units are so connected that one of them is always consuming the output of the transformer. The transformer is thus in constant use. Electric steel furnaces are an exception to this rule, in that they are often intermittently operated.

Power for electrochemical operations may be considered to be of several kinds. Direct-current power is that applied to the cell or furnace. The equivalent a.c. power takes into account losses incurred during conversion of alternating current to direct current as well as transformer losses in stepping down delivered power to the voltage at which it is fed into the alternating current end of the conversion equipment, as well as losses due to switchgear and controls. The over-all a.c. power is that actually paid for by the plant and includes the a.c. power equivalent to the direct current of the tank, cell, or furnace as well as that

1320 (1935); MORTON, L. W., and BOHN, D. I., Load Pick-up by Ignitron Rectifiers, *Trans. Am. Inst. Elec. Engrs.*, **62**, 679 (1943); FLETEMEYER, L. H., Direct-current Conversion Equipment in the Electrochemical Industry, *Trans. Electrochem. Soc.*, **81**, 103 (1942); RHEA, T. R., and ZIELINSKI, H. H., Electrical Equipment for Large Electrochemical Installations, *Trans. Am. Inst. Elec. Engrs.*, **61**, 733 (1942); SEAMAN, J. W., and MORTON, L. W., A New Multipole High-speed Anode Circuit Breaker and Its Relation to Arcback Problem, *Trans. Am. Inst. Elec. Engrs.*, **61**, 788 (1942); World's Largest Gas-engine Plant, Rated at 78,000 Kw—Powers Aluminum Works, *Power*, **88**, 64 (1944); "Power Requirement in Electrochemical, Electrometallurgical, and Allied Industries," Federal Power Commission, Washington, D.C., 1938; Cox, J. N., and BOHN, D. I., Power Rectification in Aluminum Production, *Chem. & Met. Eng.*, **48**, No. 9, 108 (1941); FRICK, C. W., A Short-cut Method of Estimating TIF of Power Systems with Rectifier Load, *Am. Inst. Elec. Engrs.*, December, 1943; "Inductive Co-ordination Aspects of Rectifier Installations," A report of the Electronic Power Conversion Subcommittee of American Institute of Electrical Engineers, Electronics Committee, May, 1946.
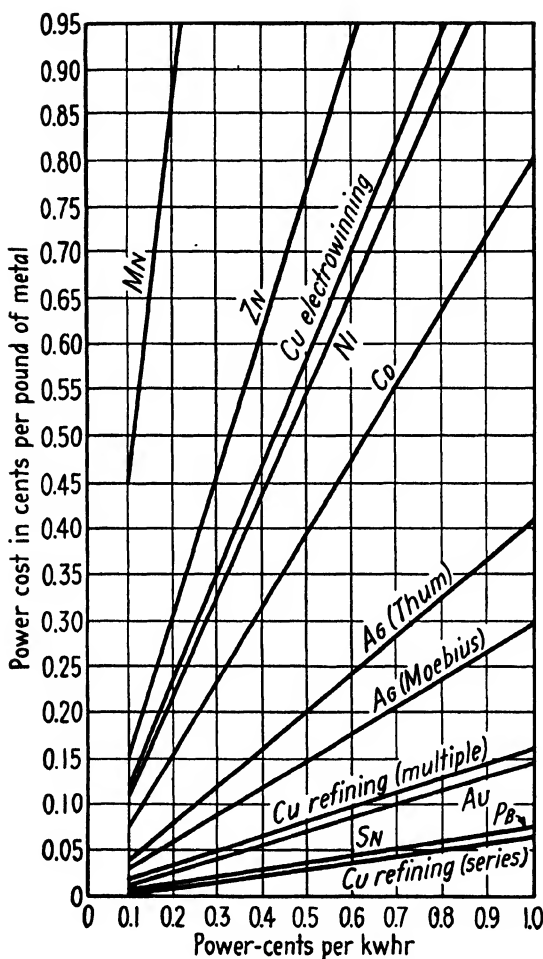
FIG. 280. Power costs for metal production.

power for auxiliaries, pumps, fans, motors, cranes, lighting, and services related to and needed for the electrolytic operation.

It is obviously misleading to apply an a.c. power cost as delivered to a d.c. power consumption for a product to determine power cost. Financial evaluation should always be on the basis of over-all a.c. power to the plant applied over the number of weight units of product per day or other time period.

Power Cost of Electrochemical Products.   Power cost is an important factor in all electrolytic or electrothermal products. Figure 280 shows the power cost in cents per pound of metal at varying power costs (in cents per kilowatthour) for the electro-
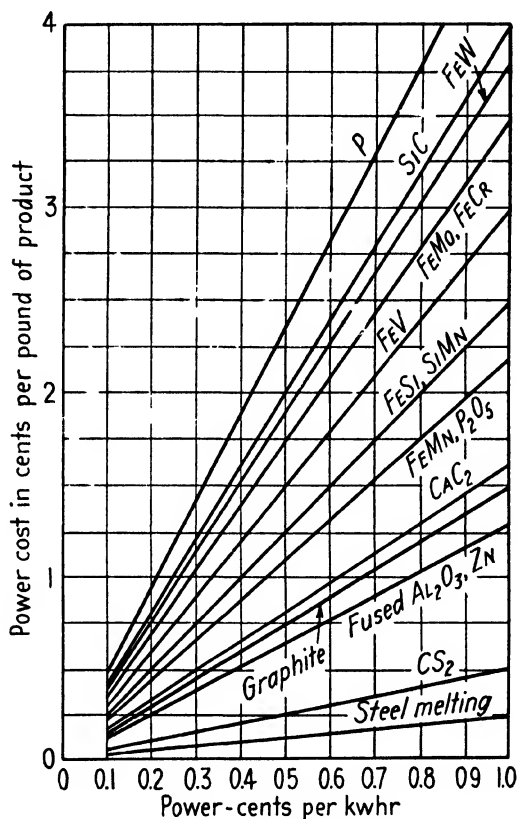
FIG. 281.   Power costs for electric-furnace products.

lytic and electrowinning industries, while Fig. 281 gives similar data for the electric-furnace products and Fig. 282 for the fused electrolytes.   The curves are plotted from the power consumptions for these products tabulated in Table 97.

Some typical power costs at various localities are given in Table 98.   Unless otherwise stated, the generation of power is in hydroelectric plants.   In the United States. electrolytic and

electrothermal plants, with the exception of copper refineries, are located where electric energy is available at low cost, at centers like Niagara Falls, N.Y.; Niagara Falls, Ont.; Massena, N.Y.; Keokuk, Iowa; Sault Ste. Marie, Mich.; Knoxville and Alcoa, Tenn.; Badin, N.C.; Charleston and the Kanawha Valley, W. Va.; and Tacoma, Wash.

Power for Electroplating.   In the special case of electroplating where power is a relatively unimportant cost, the terminal emf
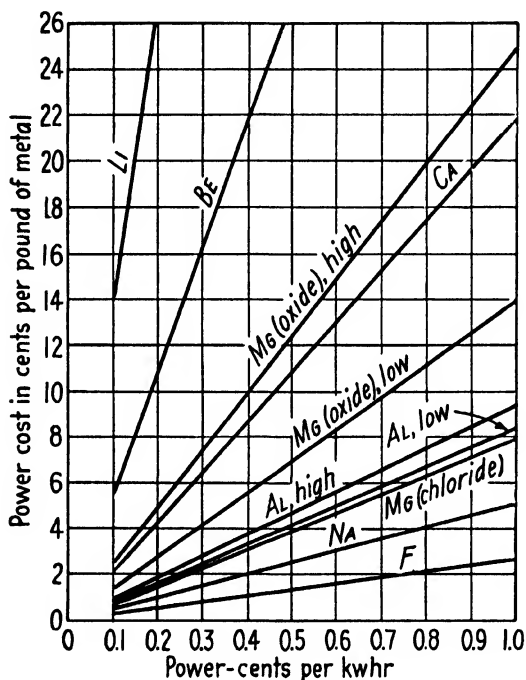
FIG. 282.   Power costs for metals from fused electrolytes.

of a plating tank is low and electroplating generators are built to supply either 6- or 12-volt high-amperage current.   Where more than 6 volts are required, it is customary to connect the two commutators of a generator in series.

Copper oxide plate-type rectifiers, consisting of one-, two-, or three-phase power transformer to transform alternating current to low voltage with an air-circulating fan and a rectifying unit

TABLE 97. ENERGY CONSUMPTION OF ELECTROCHEMICAL PRODUCTS

Industry and product	Kwhr/lb	Lb/kwhr	Voltage per tank, cell, or furnace
Electrolytic refining:			
Copper, multiple system..	0.09–0 2	5 –13 3	0 16–0 8
Copper, series system. .	0 074	13.5	
Gold (troy lb)	0.15	8 6	0 5 -2 8
Lead..... .	0 07–0.09	11.1 –14 3	0 35–0 5
Nickel ..	1.1	0 9	2 4
Silver, Moebius (troy lb)..	0 27–0 3	3.3 – 3 7	2 3 –2 8
Silver, Thum (troy lb).	0.33–0 60	1.67– 3 0	1 3 –5 4
Tin......	0.085	11.8	0 3 –0 35
Electrowinning:			
Antimony.			2.5 –3
Cadmium....	0 65–0.97	1 03– 1.54	2 5 –3 1
Copper.	0 89 -1 34	1 07– 1 12	1 96–2 16
Manganese, d.c.....	4 –4.5	2 2 – 2 5	5
Manganese, a c	5 –5.25	0 19– 0 2	
Zinc	1.4 –1.6	0 61– 0.71	3 –3.7
Metal powders:			
Iron.	1.20	0 83	2 5
Nickel	1 13	0 88	1 4 –1 5
Zinc	1 37	0 73	3.4
Fused electrolytes:			
Aluminum......	8.5 –9 5	0.11– 0 12	5 5 –6.5
Beryllium	55	0 18	5–8
Calcium.	22–24	0 04	25
Fluorine	2 8 –3 0	0.3 – 0 35	6–11
Lithium	140	0 007	8–9
Magnesium, chloride......	8	0 125	6 2
Magnesium, oxide. .	14–25	0.4 – 0 7	9–16
Sodium .	5 2	0.192	5 7 –6 0
Electric-furnace products:			
Calcium carbide ..	1 65	0.61	55–95
Carbon bisulfide	0 4 –0 5	2 – 2 5	60
Ferrochromium, 70 %. . .	3–4	0.25– 0 33	90–120
Ferromanganese, 75 % ...	2 –2 5	0 4 – 0 5	90–115
Ferromolybdenum, 50 %...	3–4	0.25– 0.33	50–150
Ferrosilicon, 50 %..	2 –3.5	0.28– 0.5	75–150
Ferrotungsten, 70 %.	3 8	0.26	90–120
Ferrovanadium, 35–45 %.......	2.3 –4	0.25– 0.44	150–250
Fused alumina.................	1.15–1.6	0.63– 0.87	100–110
Graphite..	1.5 –2	0.67	80–200
Phosphorus..	4 –5.5	0.18– 0.25	

TABLE 97. ENERGY CONSUMPTION OF ELECTROCHEMICAL PRODUCTS.—
(Continued)

Industry and product	Kwhr/lb	Lb/kwhr	Voltage per tank, cell, or furnace
P$_2$O$_5$...	2.2 –2.3	0.43– 0.45	
Silicomanganese, 70%.. .. .	2–3	0 33– 0 5	90–120
Silicon carbide. .	4 –4.7	0 21– 0.25	75–230
Steel, cold charge. . . .	0.25–0 4	2 5 – 4	75–150
Steel, hot charge.	0 05–0.2	5–20	
Zinc.....	1 28	0 78	250–275
Aqueous electrolytes:			
Caustic, mercury cells......	1 33–1.72	0.58– 0.75	3.75–5 0
Caustic, diaphragm cells..	1 04–1 47	0.68– 0.96	3 2 –4 55
Chlorates. .	2.4 –3	0 33– 0.41	2 8 –3.6
Chlorine, mercury cells.....	1.49–1 89	0 53– 0.67	3.75–5.0
Chlorine, diaphragm cells...	1 16–1.61	0 62– 0 86	3.2 –4.55
Hydrogen peroxide. . .	8	0 125	5.7
Perchlorates (from chlorates).	1 5 –1 9	0 52– 0.66	5 –6.8
Perchloric acid (60%) from HCl	11 8	0 085	8
Persulfates....	8	0 125	5.7
Potassium hydroxide . .	0 95–1 23	0 81– 1 05	4.1 –4.3

TABLE 98. TYPICAL POWER COSTS

	Cents per Kilowatthour
Alabama (steam)	0 38–0 6
Arvida, Que., Canada.	0 1 –0 15
Bonneville, Ore	0 2 –0 3
California (steam)	0.38–0.6
England..	0.4 –0 5
French Alps.	0 17–0.3
Germany (brown coal)	0 38
Knoxville, Tenn.. .. 0 42	0 42
Massena, N.Y... .	0 36
New York Harbor (steam)... .	0 67–1 3
Niagara Falls.. . . .	0 3 up
Norway	0 1 –1.5
Ontario, Canada.. ·	0.15–0.4
Scotland...... . .	0 3 –0.5
Shawinigan, Que., Canada.	0 15–0.2
Sweden..	0 1 –1 5
Switzerland...	0 3
Tennessee (steam).	0.38–0 6
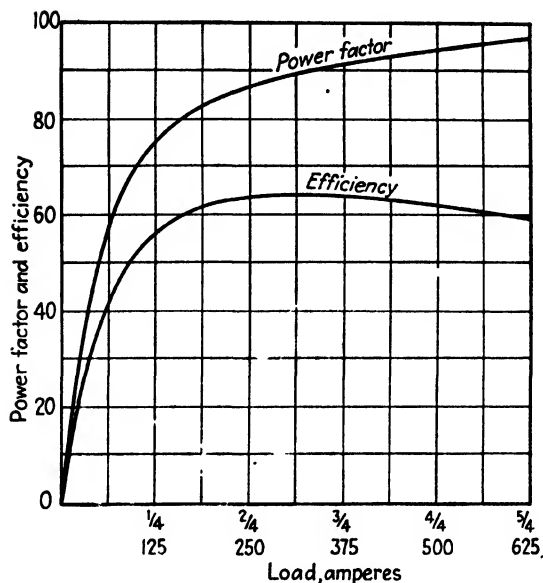
FIG. 283. Power factor and efficiency curve of a 500-amp, 6-volt copper oxide rectifier after 6 months' service.

consisting of a large number of rectangular Cu_2O rectifier plates, have found employment for electroplating operations where they replace motor-generator sets. Figure 283 shows the power factor and efficiency curve of a 500-amp, 6-volt Cu_2O rectifier after 6 months' service. Selenium rectifiers, discussed previously, are competitive.

.

APPENDIX

ELECTROCHEMICAL EQUIVALENTS

The electrochemical equivalents of the elements are tabulated. The use of the table has been simplified in that not only the ordinary valences of the elements are included, but also the changes of valence which occur in oxidation-reduction reactions. For example, while iron exhibits the valence of 2 or 3, in the reduction of ferric to ferrous iron there is a valence change of 1. In Table 99[1] valence changes of 1, when they are not a normal valence or normal valence change of the element, are indicated as n.

[1] Ro᾽ sh, G. A., *Trans. Electrochem. Soc.*, **73**, 290 (1938).

Table 99. Electrochemical Equivalents of the Elements

1	2		3	4	5	6	7	8	9
Element	Sym-bol	Atomic weight	Val. or chg. val.	Mg./coulomb	Cou-lombs /mg.	G./amp.-hr.	Amp.-hr. /g.	Lb./1,000 amp.-hr.	Amp.-hr. /lb.
Actinium	Ac	227¹	3	0.78 4$\overline{11}$	1.27 5$\overline{33}$	2.82 $\overline{280}$	0.35 4$\overline{26}$	6.22 3$\overline{20}$	160.$\overline{689}$
			n	2.35 $\overline{233}$	0.42 5$\overline{11}$	8.46 $\overline{839}$	0.11 8$\overline{09}$	18.6$\overline{6}$ 9$\overline{61}$	53.5$\overline{63}$
Alabamine	Ab	221¹	7	0.32 7$\overline{17}$	3.05 6$\overline{56}$	1.17 7$\overline{79}$	0.84 9$\overline{04}$	2.59 6$\overline{56}$	385.$\overline{120}$
			5	0.45 8$\overline{03}$	2.18 3$\overline{26}$	1.64 8$\overline{91}$	0.60 6$\overline{46}$	3.63 5$\overline{23}$	275.0$\overline{86}$
			3	0.76 3$\overline{39}$	1.30 9$\overline{95}$	2.74 8$\overline{19}$	0.36 3$\overline{88}$	6.05 8$\overline{71}$	165.0$\overline{52}$
			2	1.14 5$\overline{08}$	0.87 3$\overline{30}$	4.12 $\overline{228}$	0.24 2$\overline{58}$	9.08 8$\overline{07}$	110.0$\overline{34}$
			1	2.29 $\overline{016}$	0.43 6$\overline{65}$	8.24 $\overline{456}$	0.12 1$\overline{29}$	18.17 $\overline{614}$	55.0$\overline{17}$
Aluminum	Al	26.97	3	0.09 316	10.73 $\overline{415}$	0.33 538	2.98 1$\overline{71}$	0.73 9$\overline{38}$	1352.$\overline{480}$
			n	0.27 9$\overline{48}$	3.57 8$\overline{05}$	1.00 6$\overline{13}$	0.99 3$\overline{90}$	2.21 8$\overline{15}$	450.8$\overline{27}$
Antimony	Sb	121.76	5	0.25 235	3.96 2$\overline{72}$	0.90 847	1.10 0$\overline{75}$	2.00 2$\overline{83}$	499.29$\overline{4}$
			3	0.42 059	2.37 7$\overline{63}$	1.51 4$\overline{11}$	0.66 045	3.33 8$\overline{05}$	299.57$\overline{6}$
			2	0.63 088	1.58 5$\overline{00}$	2.27 1$\overline{17}$	0.44 030	5.00 707	199.71$\overline{7}$
			n	1.26 1$\overline{76}$	0.79 254	4.54 2$\overline{34}$	0.22 015	10.01 4$\overline{15}$	99.858
Argon	A	39.944	n	0.41 393	2.41 5$\overline{88}$	1.49 0$\overline{14}$	0.67 108	3.28 5$\overline{19}$	304.39$\overline{6}$
Arsenic	As	74.91	5	0.15 2$\overline{54}$	6.44 1$\overline{06}$	0.55 8$\overline{91}$	1.78 9$\overline{18}$	1.23 2$\overline{19}$	811.5$\overline{60}$
			3	0.25 8$\overline{76}$	3.86 4$\overline{64}$	0.93 152	1.07 3$\overline{51}$	2.05 3$\overline{66}$	486.93$\overline{6}$
			2	0.38 8$\overline{13}$	2.57 6$\overline{42}$	1.39 7$\overline{29}$	0.71 567	3.08 0$\overline{49}$	324.62$\overline{4}$
			n	0.77 627	1.28 8$\overline{21}$	2.79 457	0.35 7$\overline{84}$	6.16 0$\overline{57}$	162.3$\overline{12}$
Barium	Ba	137.36	2	0.71 171	1.40 507	2.56 2$\overline{16}$	0.39 030	5.64 8$\overline{58}$	177.03$\overline{5}$
			n	1.42 3$\overline{42}$	0.70 253	5.12 4$\overline{31}$	0.19 515	11.29 7$\overline{17}$	88.518
Beryllium	Be	9.02	2	0.04 6$\overline{74}$	21.3$\overline{9}$ 6$\overline{88}$	0.16 8$\overline{25}$	5.94 3$\overline{58}$	0.37 0$\overline{92}$	2695.9$\overline{83}$
			n	0.09 347	10.6$\overline{9}$ 8$\overline{44}$	0.33 6$\overline{50}$	2.97 1$\overline{79}$	0.74 1$\overline{85}$	1347.9$\overline{81}$
Bismuth	Bi	209.00	5	0.43 316	2.30 8$\overline{61}$	1.55 9$\overline{38}$	0.64 128	3.43 7$\overline{84}$	290.88$\overline{0}$
			3	0.72 193	1.38 5$\overline{17}$	2.59 8$\overline{96}$	0.38 477	5.72 9$\overline{73}$	174.528
			2	1.08 2$\overline{90}$	0.92 345	3.89 8$\overline{45}$	0.25 651	8.59 4$\overline{60}$	116.35$\overline{2}$
			n	2.16 5$\overline{80}$	0.46 172	7.79 6$\overline{89}$	0.12 826	17.18 9$\overline{20}$	58.176
Boron	B	10.82	5	0.02 242	44.59 3$\overline{37}$	0.08 073	12.38 7$\overline{04}$	0.17 798	5618.6$\overline{69}$
			3	0.03 737	26.75 6$\overline{02}$	0.13 455	7.43 2$\overline{23}$	0.29 662	3371.2$\overline{01}$
			2	0.05 606	17.83 7$\overline{35}$	0.20 182	4.95 4$\overline{82}$	0.44 495	2247.4$\overline{67}$
			n	0.11 21$\overline{2}$	8.91 8$\overline{67}$	0.40 365	2.47 7$\overline{41}$	0.88 989	1123.7$\overline{34}$
Bromine	Br	79.916	7	0.11 831	8.45 2$\overline{63}$	0.42 590	2.34 7$\overline{95}$	0.93 896	1065.01$\overline{3}$
			6	0.13 802	7.24 5$\overline{11}$	0.49 689	2.01 2$\overline{52}$	1.09 545	912.86$\overline{8}$
			5	0.16 563	6.03 7$\overline{59}$	0.59 626	1.67 7$\overline{08}$	1.31 454	760.72$\overline{4}$
			4	0.20 704	4.83 0$\overline{07}$	0.74 533	1.34 1$\overline{69}$	1.64 317	608.57$\overline{9}$
			3	0.27 605	3.62 2$\overline{55}$	0.99 377	1.00 6$\overline{28}$	2.19 0$\overline{90}$	456.43$\overline{4}$
			2	0.41 407	2.41 5$\overline{04}$	1.49 0$\overline{66}$	0.67 084	3.28 6$\overline{34}$	304.28$\overline{9}$
			1	0.82 815	1.20 7$\overline{52}$	2.98 132	0.33 542	6.57 2$\overline{69}$	152.14$\overline{5}$
Cadmium	Cd	112.41	2	0.58 244	1.71 6$\overline{93}$	2.09 6$\overline{77}$	0.47 692	4.62 258	216.32$\overline{9}$
			n	1.16 487	0.85 846	4.19 3$\overline{53}$	0.23 846	9.24 51$\overline{8}$	108.16$\overline{5}$

TABLE 99. ELECTROCHEMICAL EQUIVALENTS OF THE ELEMENTS.—
(*Continued*)

1		2	3	4	5	6	7	8	9
Element	Sym-bol	Atomic weight	Val. or chg.val.	Mg./coulomb	Coulombs/mg.	G./amp.-hr.	Amp.-hr./g.	Lb./1,000 amp.-hr.	Amp.-hr./lb.
Calcium	Ca	**40.08**	2	0.20 76$\overline{7}$	4.81 53$\overline{7}$	0.74 76$\overline{1}$	1.33 78$\overline{0}$	1.64 81$\overline{9}$	606.72$\overline{6}$
			n	0.41 53$\overline{4}$	2.40 76$\overline{8}$	1.49 52$\overline{1}$	0.66 88$\overline{0}$	3.29 63$\overline{8}$	303.36$\overline{3}$
Carbon	C	**12.010**	4	0.03 111	32.13 98$\overline{9}$	0.11 20$\overline{1}$	8.92 77$\overline{5}$	0.24 69$\overline{4}$	4049.55$\overline{8}$
			2	0.06 223	16 06 99$\overline{4}$	0.22 40$\overline{2}$	4.46 38$\overline{7}$	0.49 38$\overline{8}$	2024.77$\overline{9}$
			n	0.12 44$\overline{6}$	8.03 49$\overline{7}$	0.44 80$\overline{4}$	2.23 19$\overline{4}$	0.98 77$\overline{6}$	1012.39$\overline{0}$
Cerium	Ce	140.13	4	0.36 303	2.75 45$\overline{9}$	1.30 69$\overline{1}$	0.76 516	2.88 12$\overline{5}$	347.07$\overline{2}$
			3	0.48 404	2.06 59$\overline{4}$	1.74 255	0.57 387	3.84 16$\overline{6}$	260.30$\overline{4}$
			1	1.45 21$\overline{2}$	0.68 865	5.22 765	0.19 129	11.52 49$\overline{9}$	86.768
Cesium	Cs	**132.91**	1	1 37 73$\overline{1}$	0.72 606	4.95 83$\overline{0}$	0.20 168	10.93 1$\overline{1}\overline{8}$	91.481
Chlorine	Cl	35.457	7	0.05 248 9	19.0.. 12$\overline{4}$	0.18 896	5.29 20$\overline{1}$	0.41 659	2400.4$\overline{1}\overline{7}$
			6	0.06 123 8	16.32 96$\overline{4}$	0.22 046	4.53 60$\overline{1}$	0.48 603	2057 50$\overline{0}$
			5	0.07 348 6	13.60 80$\overline{3}$	0.26 455	3.78 00$\overline{1}$	0.58 323	1714.58$\overline{3}$
			4	0.09 185 8	10.88 64$\overline{2}$	0.33 069	3.02 40$\overline{1}$	0.72 904	1373.66$\overline{7}$
			3	0.12 248	8.16 48$\overline{2}$	0.44 092	2.26 80$\overline{1}$	0.97 205	1028.75$\overline{0}$
			2	0.18 372	5.44 32$\overline{1}$	0.66 137	1.51 20$\overline{0}$	1.45 80$\overline{8}$	685.83$\overline{3}$
			1	0.36 743	2.72 16$\overline{1}$	1.32 27$\overline{5}$	0.75 600	2.91 61$\overline{6}$	342.917
Chromium	Cr	52.01	6	0.08 983	10.13 2$\overline{4}\overline{7}$	0.32 33$\overline{8}$	3.09 23$\overline{5}$	0.71 29$\overline{3}$	1402.6$\overline{6}\overline{8}$
			4	0.13 47$\overline{4}$	7.42 16$\overline{5}$	0.48 50$\overline{7}$	2.06 15$\overline{7}$	1.06 93$\overline{9}$	935.1$\overline{1}\overline{2}$
			3	0.17 96$\overline{5}$	5.56 62$\overline{4}$	0.64 67$\overline{6}$	1.54 61$\overline{8}$	1.42 58$\overline{5}$	701.33$\overline{4}$
			2	0.26 94$\overline{8}$	3.71 08$\overline{2}$	0.97 01$\overline{3}$	1.03 07$\overline{8}$	2.13 87$\overline{8}$	467.55$\overline{6}$
			1	0.53 89$\overline{6}$	1.85 54$\overline{1}$	1.94 02$\overline{7}$	0.51 53$\overline{9}$	4.27 75$\overline{6}$	233.77$\overline{8}$
Cobalt	Co	58.94	3	0.20 35$\overline{9}$	4.91 17$\overline{7}$	0.73 287	1.36 45$\overline{0}$	1.61 57$\overline{0}$	618.9$\overline{2}\overline{5}$
			2	0.30 53$\overline{9}$	3.27 45$\overline{2}$	1.09 93$\overline{1}$	0.90 96$\overline{6}$	2.42 35$\overline{6}$	412.6$\overline{1}\overline{7}$
			1	0.61 07$\overline{8}$	1.63 72$\overline{6}$	2.19 86$\overline{1}$	0.45 48$\overline{3}$	4.84 7$\overline{1}\overline{1}$	206.30$\overline{8}$
Columbium	Cb	**92.91**	5	0.19 25$\overline{6}$	5.19 32$\overline{0}$	0.69 32$\overline{1}$	1.44 25$\overline{5}$	1.52 82$\overline{8}$	**654.3$\overline{3}\overline{2}$**
			4	0.24 07$\overline{0}$	4.15 45$\overline{6}$	0.86 65$\overline{2}$	1.15 40$\overline{4}$	1.91 03$\overline{5}$	**523.46$\overline{6}$**
			3	0.32 09$\overline{3}$	3.11 59$\overline{2}$	1.14 70$\overline{2}$	0.86 55$\overline{3}$	2.54 71$\overline{3}$	**392.599**
			2	0.48 14$\overline{0}$	2.07 72$\overline{8}$	1.73 30$\overline{4}$	0.57 70$\overline{2}$	3.82 05$\overline{9}$	**261.7$\overline{3}\overline{3}$**
			1	0.96 28$\overline{0}$	1.03 86$\overline{4}$	3.46 607	0.28 85$\overline{1}$	7.64 13$\overline{8}$	**130.86$\overline{6}$**
Copper	Cu	63.57	2	0.32 93$\overline{8}$	3.03 60$\overline{2}$	1.18 57$\overline{6}$	0.84 33$\overline{4}$	2.61 41$\overline{6}$	382.5$\overline{3}\overline{2}$
			1	0.65 87$\overline{6}$	1.51 80$\overline{1}$	2.37 15$\overline{2}$	0.42 167	5.22 83$\overline{1}$	191.2$\overline{6}\overline{6}$
Dysprosium	Dy	162.46	3	0.56 069	1.78 35$\overline{1}$	2.01 84$\overline{9}$	0.49 542	4.44 90$\overline{1}$	224.88$\overline{6}$
			n	1.68 207	0.59 450	6.05 547	0.16 514	13.34 00$\overline{2}$	74.962
Erbium	Er	167.2	3	0.57 75$\overline{5}$	1.73 14$\overline{5}$	2.07 9$\overline{1}\overline{7}$	0.48 09$\overline{6}$	4.58 37$\overline{8}$	218.1$\overline{6}\overline{0}$
			n	1.73 26$\overline{4}$	0.57 71$\overline{5}$	6.23 75$\overline{1}$	0.16 03$\overline{2}$	13.75 1$\overline{3}\overline{5}$	72.72$\overline{0}$
Europium	Eu	152.0	3	0.52 50$\overline{4}$	1.90 48$\overline{1}$	1.89 01$\overline{6}$	0.52 90$\overline{6}$	4.16 70$\overline{8}$	241.9$\overline{1}\overline{1}$
			n	1.57 51$\overline{3}$	0.63 487	5.67 04$\overline{7}$	0.17 63$\overline{5}$	12.40 1$\overline{2}\overline{4}$	80.637

TABLE 99. ELECTROCHEMICAL EQUIVALENTS OF THE ELEMENTS.—
(*Continued*)

1	2	3	4	5	6	7	8	9
Element	Symbol	Atomic weight	Val. or chg. val.	Mg./coulomb	Coulombs/mg.	G./amp.-hr.	Amp.-hr./g.	Lb./1,000 amp.-hr.	Amp.-hr./lb.
Fluorine........	F	19.00	1	0.19 689	5.07 895	0.70 881	1.41 082	1.56 265	639.937
Gadolinium.....	Gd	**156.9**	3	0.54 179	1.84 572	1.95 046	0.51 270	4.30 002	232.737
			n	1.62 538	0.61 524	5.85 137	0.17 090	12.90 007	77.579
Gallium.........	Ga	69.72	3	0.24 083	4.15 232	0.86 698	1.15 342	1.91 137	523.184
			2	0.36 124	2.76 822	1.30 048	0.76 895	2.86 706	348.789
			1	0.72 249	1.38 411	2.60 095	0.38 447	5.73 412	174.395
Germanium.....	Ge	72.60	4	0.18 808	5.31 680	0.67 710	1.47 689	1.49 275	669.906
			2	0.37 617	2.65 840	1.35 420	0.73 845	2.98 549	334.953
			n	0.75 233	1.32 920	2.70 839	0.36 922	5.97 099	167.476
Gold............	Au	197.2	3	0.68 117	1.46 805	2.45 223	0.40 779	5.40 624	184.972
			2	1.02 176	0.97 870	3.67 834	0.27 186	8.10 936	123.314
			1	2.04 352	0.48 935	7.35 668	0.13 593	16.21 871	61.657
Hafnium ..	Hf	178.6	4	0.46 269	2.16 125	1.66 570	0.60 035	3.67 223	272.313
			n	1.85 078	0.54 031	6.66 280	0.15 009	14.68 895	68.078
Helium.........	He	4.003	n	0.04 148 2	24.10 692	0.14 933	6.69 637	0.32 923	3037.421
Holmium ..	Ho	163.5	3	0.56 477	1.77 064	2.03 316	0.49 185	4.48 235	223.097
			n	1.69 430	0.59 021	6.09 948	0.16 395	13.44 705	74.366
Hydrogen	H	1.0081	1	0.01 044 7	95.72 465	0.03 760 8	26.59 018	0.08 291	12061.102
Deuterium²....	D	**2.01471**	1	0.02 087 8	47.89 771	0.07 516 0	13.30 492	0.16 570	6035.011
Illinium........	Il	**146**¹	3	0.50 432	1.98 288	2.72 332	0.55 080	3.90 256	272.539
			n	1.51 295	0.66 096	5.44 663	0.18 360	11.00 760	90.846
Indium..	In	**114.76**	3	0.39 641	2.52 266	1.42 707	0.70 074	3.14 614	317.849
			n	1.18 922	0.84 089	4.28 120	0.23 358	9.43 843	105.950
Iodine...	I	**126.92**	7	0.18 790	5.32 225	0.67 641	1.47 840	1.49 122	670.593
			6	0.21 921	4.56 193	0.78 914	1.26 720	1.73 976	574.794
			5	0.26 305	3.80 161	0.94 697	1.05 600	2.08 771	478.995
			4	0.32 881	3.04 129	1.18 371	0.84 480	2.60 963	383.196
			3	0.43 841	2.28 096	1.57 828	0.63 360	3.47 951	287.397
			2	0.65 762	1.52 064	2.36 742	0.42 240	5.21 927	191.598
			1	1.31 523	0.76 032	4.73 484	0.21 120	10.43 853	95.799
Iridium.........	Ir	193.1	4	0.50 026	1.99 896	1.80 095	0.55 546	3.97 038	251.865
			3	0.66 701	1.49 922	2.40 134	0.41 659	5.29 384	188.899
			1	2.00 104 ·	0.49 974	7.20 373	0.13 886	15.88 151	62.966
Iron............	Fe	55.84	3	0.19 288	5.18 446	0.69 438	1.44 013	1.53 085	653.230
			2	0.28 933	3.45 630	1.04 158	0.96 008	2.29 628	435.487
			1	0.57 865	1.72 815	2.08 315	0.48 004	4.59 256	217.774

TABLE 99. ELECTROCHEMICAL EQUIVALENTS OF THE ELEMENTS.—
(*Continued*)

1	2	3	4	5	6	7	8	9
Element	Symbol	Atomic weight	Val. or chg. val.	Mg./coulomb	Coulombs/mg.	G./amp.-hr.	Amp.-hr./g.	Lb./1,000 amp.-hr.	Amp.-hr/lb.
Krypton........	Kr	**83.7**	n	0.86 73$\overline{6}$	1.15 2$\overline{93}$	3.12 $\overline{249}$	0.32 0$\overline{26}$	6.88 $\overline{390}$	145.2$\overline{86}$
Lanthanum......	La	**138.92**	3	0.47 986	2.08 39$\overline{3}$	1.72 75$\overline{0}$	0.57 887	3.80 84$\overline{9}$	262.57$\overline{1}$
			n	1.43 95$\overline{0}$	0.69 464	5.18 25$\overline{1}$	0.19 296	11.42 5$\overline{47}$	87.524
Lead............	Pb	**207.21**	4	0.53 681	1.86 28$\overline{4}$	1.93 25$\overline{3}$	0.51 746	4.26 05$\overline{0}$	234.71$\overline{5}$
			2	1.07 36$\overline{3}$	0.93 142	3.86 50$\overline{6}$	0.25 873	8.52 09$\overline{9}$	117.35$\overline{7}$
			1	2.14 72$\overline{5}$	0.46 571	7.73 01$\overline{1}$	0 12 936	17.04 1$\overline{98}$	58.679
Lithium.........	Li	6.940	1	0.07 192	13.90 $\overline{190}$	0.25 89$\overline{0}$	3.86 2$\overline{47}$	0.57 078	1751.5$\overline{88}$
Lutecium...... .	Lu	175.0	3	0.60 44$\overline{9}$	1.65 4$\overline{29}$	3.26 4$\overline{25}$	0.45 95$\overline{2}$	7.34 87$\overline{4}$	208.4$\overline{37}$
			n	1.81 3$\overline{47}$	0.55 1$\overline{43}$	6.52 8$\overline{49}$	0.15 317	14.39 $\overline{287}$	69.47$\overline{5}$
Magnesium..	Mg	24.32	2	0.12 60$\overline{1}$	7.93 58$\overline{6}$	0.45 36$\overline{4}$	2.20 4$\overline{40}$	1.00 0$\overline{10}$	999.90$\overline{1}$
			n	.25 20$\overline{2}$	3.96 79$\overline{3}$	0 90 727	1.10 2$\overline{20}$	2.00 0$\overline{20}$	499.95$\overline{1}$
Manganese. ...	Mn	54.93	7	0.08 132	12.29 77$\overline{2}$	0.29 27$\overline{4}$	3.41 60$\overline{3}$	0.64 537	1549.$\overline{487}$
			6	0.09 487	10.54 0$\overline{50}$	0.34 15$\overline{3}$	2.92 80$\overline{3}$	0.75 294	1328.1$\overline{32}$
			5	0.11 38$\overline{1}$	8.78 4$\overline{05}$	0.50 983	2.44 00$\overline{2}$	0.90 35$\overline{2}$	1106.777
			4	0.14 23$\overline{0}$	7.02 72$\overline{7}$	0.51 229	1.95 20$\overline{2}$	1.12 94$\overline{1}$	885.42$\overline{1}$
			3	0.18 97$\overline{1}$	5.27 0$\overline{45}$	0.68 305	1.46 40$\overline{1}$	1.50 58$\overline{7}$	664.06$\overline{6}$
			2	0.28 46$\overline{1}$	3.51 36$\overline{3}$	1.02 45$\overline{8}$	0.97 60$\overline{1}$	2.25 88$\overline{1}$	442.71$\overline{1}$
			1	0.56 92$\overline{1}$	1.75 68$\overline{2}$	2.04 91$\overline{6}$	0.48 80$\overline{0}$	4.51 7$\overline{62}$	221.35$\overline{5}$
Masurium ...	Ma	**97.8**⁽	7	0.14 47$\overline{8}$	6.90 $\overline{095}$	0.52 12$\overline{1}$	1.91 $\overline{860}$	1.14 $\overline{908}$	870.2$\overline{62}$
			n	1.01 3$\overline{47}$	0.98 67$\overline{1}$	3.64 8$\overline{50}$	0.27 40$\overline{9}$	8.04 3$\overline{56}$	124.3$\overline{23}$
Mercury........	Hg	200.61	2	1.03 94$\overline{3}$	0.96 207	3.74 195	0.26 724	8.24 958	121.21$\overline{8}$
			1	2.07 88$\overline{6}$	0.48 103	7.48 39$\overline{0}$	0.13 362	16.49 91$\overline{7}$	60.609
Molybdenum....	Mo	95.95	6	0.16 57$\overline{2}$	6.03 43$\overline{9}$	0.59 658	1.67 62$\overline{2}$	1.31 52$\overline{3}$	760.32$\overline{1}$
			5	0.19 88$\overline{6}$	5.02 86$\overline{6}$	0.71 59$\overline{0}$	1.39 68$\overline{5}$	1.57 82$\overline{8}$	633.60$\overline{1}$
			4	0.24 85$\overline{8}$	4.02 29$\overline{3}$	0.89 487	1.11 74$\overline{8}$	1.97 28$\overline{5}$	506.88$\overline{1}$
			3	0.33 14$\overline{3}$	3.01 72$\overline{0}$	1.19 31$\overline{6}$	0.83 81$\overline{1}$	2.63 0$\overline{47}$	380.16$\overline{0}$
			2	0.49 715	2.01 14$\overline{6}$	1.78 97$\overline{4}$	0.55 87$\overline{4}$	3.94 57$\overline{0}$	253.44$\overline{0}$
			1	0.99 43$\overline{0}$	1.00 57$\overline{3}$	3.57 94$\overline{8}$	0.27 937	7.89 14$\overline{1}$	126.72$\overline{0}$
Neodymium....	Nd	144.27	3	0.49 834	2.00 66$\overline{5}$	1.79 40$\overline{3}$	0.55 74$\overline{0}$	3.95 51$\overline{6}$	252.83$\overline{4}$
			n	1.49 50$\overline{3}$	0.66 888	5.38 20$\overline{9}$	0.18 580	11.86 5$\overline{48}$	84.278
Neon..........	Ne	20.183	n	0.20 915	4.78 12$\overline{5}$	0.75 294	1.32 81$\overline{3}$	1.65 99$\overline{5}$	602.42$\overline{8}$
Nickel..........	Ni	58.69	3	0.20 27$\overline{3}$	4.93 27$\overline{0}$	0.72 98$\overline{2}$	1.37 0$\overline{19}$	1.60 89$\overline{9}$	621.50$\overline{9}$
			2	0.30 40$\overline{9}$	3.28 84$\overline{6}$	1.09 47$\overline{4}$	0.91 34$\overline{6}$	2.41 3$\overline{48}$	414.34$\overline{0}$
			1	0.60 81$\overline{9}$	1.64 4$\overline{23}$	2.18 9$\overline{47}$	0.45 67$\overline{3}$	4.82 6$\overline{96}$	207.17$\overline{0}$
Nitrogen........	N	14.008	5	0.02 903 2	34.44 44$\overline{6}$	0.10 452	9.56 79$\overline{5}$	0.23 042	438.99$\overline{5}$
			4	0.03 629 0	27.55 5$\overline{58}$	0.13 064	7.65 43$\overline{8}$	0.28 802	347.19$\overline{6}$
			3	0.04 838 7	20.66 67$\overline{6}$	0.17 419	5.74 07$\overline{7}$	0.38 403	260.397
			2	0.07 258 0	13.77 78$\overline{4}$	0.26 129	3.82 71$\overline{8}$	0.57 604	173.59$\overline{8}$
			1	0.14 516	6.88 89$\overline{2}$	0.52 258	1.91 35$\overline{9}$	1.15 20$\overline{9}$	86.799

TABLE 99.   ELECTROCHEMICAL EQUIVALENTS OF THE ELEMENTS.—
(*Continued*)

1	2	3	4	5	6	7	8	9
Element	Symbol	Atomic weight	Val. or chg. val.	Mg./coulomb	Coulombs/mg.	G./amp.-hr.	Amp.-hr./g.	Lb./1,000 amp.-hr.	Amp.-hr./lb.
Osmium....	Os	190.2	8	0.24 63$\overline{7}$	4.05 85$\overline{9}$	0.88 69$\overline{4}$	1.12 74$\overline{7}$	1.95 53$\overline{7}$	447.48$\overline{5}$
			6	0.32 85$\overline{0}$	3.04 41$\overline{6}$	1.18 25$\overline{9}$	0.84 56$\overline{0}$	2.60 71$\overline{7}$	383.55$\overline{8}$
			5	0.39 42$\overline{0}$	2.53 68$\overline{0}$	1.41 9$\overline{11}$	0.70 46$\overline{7}$	3.12 88$\overline{0}$	319.63$\overline{2}$
			4	0.49 27$\overline{5}$	2.02 9$\overline{44}$	1.77 38$\overline{9}$	0.56 37$\overline{3}$	3.91 07$\overline{5}$	255.70$\overline{6}$
			3	0.65 70$\overline{0}$	1.52 20$\overline{8}$	2.36 51$\overline{8}$	0.42 28$\overline{0}$	5.21 43$\overline{3}$	191.77$\overline{9}$
			2	0.98 54$\overline{9}$	1.01 47$\overline{2}$	3.54 777	0.28 18$\overline{7}$	7.82 15$\overline{0}$	127.85$\overline{3}$
			1	1.97 09$\overline{8}$	0.50 73$\overline{6}$	7.09 55$\overline{4}$	0.14 09$\overline{3}$	15.64 2$\overline{99}$	63.92$\overline{6}$
Oxygen...... ..	O	16.0000	2	0.08 290 2	12.06 25$\overline{0}$	0.29 845	3.35 06$\overline{9}$	0.65 796	1519.85$\overline{0}$
			n	0.16 580	6.03 12$\overline{5}$	0.59 689	1.67 53$\overline{5}$	1.31 59$\overline{2}$	759.92$\overline{5}$
Palladium. ..	Pd	106.7	4	0.27 64$\overline{2}$	3.61 76$\overline{2}$	0.99 51$\overline{3}$	1.00 48$\overline{9}$	2.19 38$\overline{8}$	455.81$\overline{2}$
			3	0.36 857	2.71 33$\overline{2}$	1.32 68$\overline{4}$	0.75 367	2.92 51$\overline{8}$	340.85$\overline{9}$
			2	0.55 285	1.80 88$\overline{1}$	1.99 02$\overline{6}$	0.50 24$\overline{5}$	4.38 777	227.90$\overline{6}$
			1	1.10 57$\overline{0}$	0.90 44$\overline{0}$	3.98 05$\overline{2}$	0.25 12$\overline{2}$	8.77 55$\overline{4}$	113.95$\overline{3}$
Phosphorus ..	P	31.02	5	0.06 429	15.55 4$\overline{48}$	0.23 14$\overline{4}$	4.32 06$\overline{9}$	0.51 025	1959.83$\overline{2}$
			3	0.10 71$\overline{5}$	9.33 26$\overline{9}$	0.38 57$\overline{4}$	2.59 24$\overline{1}$	0.85 04$\overline{1}$	1175.89$\overline{9}$
			2	0.16 07$\overline{3}$	6.22 17$\overline{9}$	0.57 86$\overline{1}$	1.72 82$\overline{8}$	1.27 56$\overline{2}$	783.93$\overline{3}$
			n	0.32 14$\overline{5}$	3.11 09$\overline{0}$	1.15 72$\overline{2}$	0.86 41$\overline{4}$	2.55 12$\overline{4}$	391.96$\overline{6}$
Platinum . .	Pt	195.23	4	0.50 578	1.97 71$\overline{6}$	1.82 08$\overline{0}$	0.54 921	4.01 417	249.11$\overline{7}$
			2	1.01 15$\overline{5}$	0.98 858	3.64 16$\overline{0}$	0.27 46$\overline{0}$	8.02 83$\overline{4}$	124.55$\overline{9}$
			n	2.02 31$\overline{1}$	0.49 42$\overline{9}$	7.28 31$\overline{9}$	0.13 73$\overline{0}$	16.05 66$\overline{9}$	62.27$\overline{9}$
Polonium .	Po	210^1	6	0.36 26$\overline{9}$	2.75 71$\overline{4}$	1.30 57$\overline{0}$	0.76 58$\overline{7}$	2.87 85$\overline{7}$	347.39$\overline{4}$
			4	0.54 40$\overline{4}$	1.83 81$\overline{0}$	1.95 85$\overline{5}$	0.51 05$\overline{8}$	4.31 78$\overline{6}$	231.59$\overline{6}$
			2	1.08 80$\overline{8}$	0.91 90$\overline{5}$	3.91 71$\overline{0}$	0.25 52$\overline{9}$	8.63 57$\overline{2}$	115.79$\overline{8}$
			n	2.17 61$\overline{7}$	0.45 95$\overline{2}$	7.83 42$\overline{0}$	0.12 76$\overline{5}$	17.27 1$\overline{45}$	57.89$\overline{9}$
Potassium	K	39.096	1	0.40 514	2.46 82$\overline{8}$	1.45 85$\overline{0}$	0.68 563	3.21 54$\overline{5}$	310.99$\overline{8}$
Praseodymium...	Pr	140.92	3	0.48 677	2.05 43$\overline{6}$	1.75 23$\overline{7}$	0.57 065	3.86 33$\overline{2}$	258.845
			n	1.46 03$\overline{1}$	0.68 47$\overline{9}$	5.25 71$\overline{2}$	0.19 022	11.58 99$\overline{6}$	86.282
Protoactinium...	Pa	231	5	0.59 84$\overline{5}$	2.08 87$\overline{4}$	1.72 35$\overline{2}$	0.58 02$\overline{1}$	3.79 97$\overline{2}$	263.17$\overline{7}$
			3	0.79 79$\overline{3}$	1.25 32$\overline{5}$	2.87 25$\overline{4}$	0.34 81$\overline{2}$	6.33 28$\overline{6}$	157.90$\overline{6}$
			2	1.19 68$\overline{9}$	0.83 55$\overline{0}$	4.30 88$\overline{1}$	0.23 20$\overline{8}$	9.49 92$\overline{9}$	105.27$\overline{1}$
			n	2.39 37$\overline{8}$	0.41 77$\overline{5}$	8.61 76$\overline{2}$	0.11 60$\overline{4}$	18.99 85$\overline{9}$	52.63$\overline{5}$
Radium.........	Ra	226.05	2	1.17 12$\overline{4}$	0.85 379	4.21 64$\overline{8}$	0.23 716	9.29 57$\overline{4}$	107.57$\overline{6}$
			n	2.34 24$\overline{9}$	0.42 690	8.43 29$\overline{5}$	0.11 858	18.59 1$\overline{48}$	53.788
Radon	Rn	222	n	2.30 05$\overline{2}$	0.43 46$\overline{8}$	8.28 18$\overline{7}$	0.12 075	18.2$\overline{5}$ 83$\overline{9}$	54.76$\overline{9}$
Rhenium....	Re	186.31	7	0.27 581	3.62 56$\overline{8}$	0.99 292	1.00 71$\overline{3}$	2.18 90$\overline{1}$	456.82$\overline{8}$
			6	0.32 178	3.10 77$\overline{2}$	1.15 84$\overline{0}$	0.86 326	2.55 38$\overline{4}$	391.567
			5	0.38 613	2.58 97$\overline{7}$	1.39 00$\overline{8}$	0.71 938	3.06 46$\overline{1}$	326.30$\overline{6}$
			4	0.48 267	2.07 18$\overline{2}$	1.73 76$\overline{1}$	0.57 550	3.83 077	261.04$\overline{4}$
			3	0.64 356	1.55 38$\overline{6}$	2.31 68$\overline{1}$	0.43 163	5.10 769	195.78$\overline{3}$
			2	0.96 537	1.03 59$\overline{1}$	3.47 52$\overline{1}$	0.28 775	7.66 15$\overline{3}$	130.52$\overline{2}$
			1	1.93 067	0.51 795	6.95 04$\overline{2}$	0.14 388	15.32 30$\overline{6}$	65.261

TABLE 99. ELECTROCHEMICAL EQUIVALENTS OF THE ELEMENTS.—
(*Continued*)

1		2	3	4	5	6	7	8	9
Element	Symbol	Atomic weight	Val. or chg. val.	Mg./coulomb	Coulombs/mg.	G./amp.-hr.	Amp.-hr./g.	Lb./1,000 amp.-hr.	Amp.-hr./lb.
Rhodium	Rh	102.91	4	0.26 661	3.75 085̅	0.95 978	1.04 19̅0	2.11 59̅6	472.599̅
			3	0.35 547	2.81 31̅4	1.27 97̅	0.78 143	2.82 12̅8	354.44̅9
			2	0.53 321	1.87 54̅3	1.91 95̅8	0.52 095	4.23 19̅2	236.30̅0
			1	1.06 64̅2	0 93 771	3.83 91̅3	0.26 048	8.46 38̅3	118.15̅0
Rubidium	Rb	**85.48**	1	0.88 58̅0	1.12 89̅2	3.18 88̅9	0.31 359	7.03 03̅0	142.24̅1
Ruthenium	Ru	101.7	8	0.13 17̅4	7.59 09̅5	0.47 425	2.10 88̅0	1.04 55̅4	856.44̅4
			6	0.17 56̅5	5.69 32̅2	0.63 233	1.58 14̅5	1.39 40̅5	717.33̅3
			5	0.21 07̅8	4.74 47̅3	0.75 88̅0	1.31 78̅7	1.67 28̅6	597.77̅8
			4	0 26 34̅7	3.79 54̅8	0.94 85̅0	1.05 43̅0	2.09 10̅8	478.22̅2
			3	0.35 13̅0	2.84 66̅1	1 26 46̅6	0.79 07̅2	2.78 81̅0	358.66̅7
			2	0.52 69̅4	1.8. 77̅4	1.89 69̅9	0.52 71̅5	4.18 21̅6	239.11̅1
			1	1.05 38̅9	0.94 887	3.79 39̅9	0.26 357	8.36 43̅1	119.55̅6
Samarium	Sm	150.43	3	0.51 962	1.92 44̅8	1.87 06̅3	0.53 458	4.12 40̅4	242.48̅1
			n	1.55 88̅6	0.64 149	5.61 19̅0	0.17 819	12.37 21̅1	80.827̅
Scandium	Sc	45.10	3	0.15 57̅9	6.41 90̅7	0.56 08̅3	1.78 30̅7	1.23 64̅2	808.78̅9
			n	0.46 73̅6	2.13 96̅9	1.68 24̅9	0.59 43̅6	3.70 92̅5	269.59̅6
Selenium	Se	**78.96**	6	0.13 637	7.33 28̅3	0.49 09̅4	2.03 69̅0	1.08 23̅4	923.92̅1
			4	0.20 45̅6	4.88 85̅5	0.73 64̅1	1.35 79̅3	1.62 35̅2	615.94̅7
			2	0.40 91̅2	2.44 42̅8	1.47 28̅3	0.67 897	3.24 70̅3	307.97̅4
			n	0.81 82̅4	1.22 21̅4	2.94 56̅6	0.33 948	6.49 40̅6	153.98̅7
Silicon	Si	28.06	4	0.07 269	13.75 62̅4	0.26 17̅0	3.82 11̅8	0.57 695	1733.25̅7
			n	0.29 07̅8	3.43 90̅6	1.04 68̅0	0.95 52̅9	2.30 77̅9	433.31̅4
Silver	Ag	107.880	1	1.11 79̅3³	0.89 451	4.02 45̅4	0.24 848	8.87 25̅9	112.70̅7
Sodium	Na	22.997	1	0.23 831	4.19 62̅0	0.85 792	1.16 56̅1	1.89 13̅9	528.71̅2
Strontium	Sr	87.63	2	0.45 40̅4	2.20 24̅4	1.63 45̅5	0.61 17̅9	3.60 35̅6	277.50̅3
			n	0.90 808	1.10 12̅2	3.26 91̅0	0.30 58̅9	7.20 71̅3	138.75̅2
Sulphur	S	32.06	7	0.04 746	21.06 98̅7	0.17 08̅6	5.85 27̅4	0.37 668	2654.75̅9
			6	0.05 537	18.05 98̅9	0.19 93̅4	5.01 66̅4	0.43 94̅6	2275.50̅8
			5	0.06 645	15.04 99̅1	0.23 92̅0	4.18 05̅3	0.52 73̅6	1896.25̅7
			4	0.08 306	12.03 99̅3	0.29 90̅1	3.34 44̅2	0.65 91̅9	1517.00̅5
			3	0.11 07̅4	9.02 99̅4	0.39 867	2.50 83̅2	0.87 89̅2	1137.75̅4
			2	0.16 61̅1	6.01 99̅6	0.59 80̅1	1.67 23̅1	1.31 83̅9	758.50̅3
			1	0.33 22̅3	3.00 99̅8	1.19 60̅2	0.83 61̅1	2.63 677	379.25̅1
Tantalum	Ta	**180.88**	5	0.37 488	2.66 75̅1	1.34 957	0.74 098	2.97 52̅9	336.10̅1
			4	0.46 860	2.13 40̅1	1.68 69̅6	0.59 278	3.71 91̅2	268.88̅1
			3	0.62 480	1.60 05̅1	2.24 92̅8	0.44 459	4.95 88̅2	201.66̅1
			2	0.93 720	1.06 70̅1	3.37 39̅3	0.29 639	7.43 82̅4	134.44̅0
			1	1.87 44̅0	0.53 350	6.74 78̅5	0.14 820	14.87 64̅7	67.220

TABLE 99. ELECTROCHEMICAL EQUIVALENTS OF THE ELEMENTS.—
(*Continued*)

1	2	3	4	5	6	7	8	9
Element	Sym-bol	Atomic weight	Val. or chg. val.	Mg./coulomb	Coulombs /mg.	G./amp.-hr.	Amp.-hr. /g.	Lb./1,000 amp.-hr.	Amp.-hr. /lb.
Tellurium.......	Te	**127.61**	6	0.22 040	4.53 72$\overline{6}$	0.79 343	1.26 03$\overline{7}$	1.74 92$\overline{1}$	571.68$\overline{6}$
			4	0.33 060	3.02 48$\overline{4}$	1.19 01$\overline{5}$	0.84 023	2.62 38$\overline{2}$	381.12$\overline{4}$
			2	0.66 119	1.51 24$\overline{2}$	2.38 02$\overline{9}$	0.42 012	5.24 76$\overline{4}$	190.56$\overline{2}$
			n	1.32 23$\overline{8}$	0.75 621	4.76 05$\overline{8}$	0.21 006	10.49 52$\overline{8}$	95.281
Terbium........	Tb	159.2	3	0.54 99$\overline{1}$	1.81 84$\overline{7}$	1.97 96$\overline{9}$	0.50 51$\overline{3}$	4.36 44$\overline{7}$	229.1$\overline{13}$
			n	1.64 97$\overline{4}$	0.60 61$\overline{6}$	5.93 90$\overline{7}$	0.16 83$\overline{8}$	13.09 3$\overline{40}$	76.37$\overline{1}$
Thallium........	Tl	204.39	3	0.70 601	1.41 64$\overline{1}$	2.54 16$\overline{4}$	0.39 345	5.59 00$\overline{2}$	178.57$\overline{1}$
			1	2.11 80$\overline{3}$	0.47 214	7.62 49$\overline{1}$	0.13 115	16.80 00$\overline{5}$	59.524
Thorium........	Th	232.12	4	0.60 135	1.66 29$\overline{3}$	2.16 48$\overline{5}$	0.46 193	4.77 26$\overline{8}$	209.52$\overline{6}$
			n	2.40 53$\overline{9}$	0.41 573	8.65 94$\overline{0}$	0.11 548	19.09 07$\overline{0}$	52.382
Thulium........	Tm	169.4	3	0.58 51$\overline{5}$	1.70 89$\overline{7}$	2.10 65$\overline{3}$	0.47 47$\overline{1}$	4.64 41$\overline{0}$	215.3$\overline{27}$
			n	1.75 54$\overline{4}$	0.56 96$\overline{6}$	6.31 95$\overline{9}$	0.15 82$\overline{4}$	13.93 2$\overline{30}$	71.77$\overline{6}$
Tin.............	Sn	118.70	4	0.30 751	3.25 19$\overline{0}$	1.10 70$\overline{5}$	0.90 330	2.44 06$\overline{2}$	409.73$\overline{2}$
			2	0.61 503	1.62 59$\overline{5}$	2.21 40$\overline{9}$	0.45 165	4.88 12$\overline{4}$	204.86$\overline{6}$
			n	1.23 00$\overline{5}$	0.81 297	4.42 81$\overline{9}$	0.22 583	9.76 24$\overline{8}$	102.43$\overline{3}$
Titanium........	Ti	47.90	4	0.12 40$\overline{9}$	8.05 84$\overline{6}$	0.44 67$\overline{4}$	2.23 84$\overline{6}$	0.98 48$\overline{8}$	1015.$\overline{348}$
			3	0.16 54$\overline{6}$	6.04 38$\overline{4}$	0.59 56$\overline{5}$	1.67 88$\overline{4}$	1.31 31$\overline{8}$	761 5$\overline{11}$
			1	0.49 63$\overline{7}$	2.01 46$\overline{1}$	1.78 69$\overline{4}$	0.55 96$\overline{1}$	3.93 95$\overline{3}$	353.83$\overline{7}$
Tungsten..	W	183.92	6	0.31 765	3.14 81$\overline{1}$	1.14 35$\overline{4}$	0.87 447	2.52 10$\overline{8}$	396.65$\overline{5}$
			5	0.38 118	2.62 34$\overline{2}$	1.37 22$\overline{5}$	0.72 873	3.02 53$\overline{0}$	330.54$\overline{6}$
			4	0.47 648	2.09 87$\overline{4}$	1.71 53$\overline{2}$	0.58 298	3.78 16$\overline{2}$	264.43$\overline{7}$
			3	0.63 530	1.57 40$\overline{5}$	2.28 70$\overline{0}$	0.43 724	5.04 21$\overline{7}$	198.327
			2	0.95 295	1.04 93$\overline{7}$	3.43 06$\overline{3}$	0.29 149	7.56 32$\overline{5}$	132.21$\overline{8}$
			1	1.90 59$\overline{1}$	0.52 46$\overline{8}$	6.86 12$\overline{6}$	0.14 575	15.12 65$\overline{0}$	66.109
Uranium........	U	**238.07**	6	0.41 117	2.43 20$\overline{6}$	1.48 02$\overline{3}$	0.67 557	3.26 16$\overline{8}$	306.59$\overline{1}$
			5	0.49 341	2.02 67$\overline{1}$	1.77 627	0.56 298	3.91 60$\overline{1}$	255.49$\overline{2}$
			4	0.61 676	1.62 13$\overline{7}$	2.22 03$\overline{4}$	0.45 038	4.89 25$\overline{2}$	204.39$\overline{4}$
			3	0.82 235	1.21 60$\overline{3}$	2.96 04$\overline{6}$	0.33 779	6.52 33$\overline{5}$	153.29$\overline{5}$
			2	1.23 35$\overline{2}$	0.81 069	4.44 06$\overline{8}$	0.22 519	9.78 50$\overline{3}$	102.197
			1	2.46 70$\overline{5}$	0.40 534	8.88 137	0.11 260	19.57 00$\overline{6}$	51.098
Vanadium.......	V	**50.95**	5	0.10 56$\overline{0}$	9.47 00$\overline{7}$	0.38 01$\overline{5}$	2.63 05$\overline{7}$	0.83 80$\overline{8}$	1193.2$\overline{09}$
			4	0.13 19$\overline{9}$	7.57 60$\overline{6}$	0.47 51$\overline{8}$	2.10 44$\overline{6}$	1.04 76$\overline{0}$	954.56$\overline{7}$
			3	0.17 59$\overline{9}$	5.68 20$\overline{4}$	0.63 35$\overline{8}$	1.57 83$\overline{4}$	1.39 67$\overline{9}$	715.92$\overline{5}$
			2	0.26 39$\overline{9}$	3.78 80$\overline{3}$	0.95 03$\overline{6}$	1.05 22$\overline{3}$	2.09 51$\overline{9}$	477.28$\overline{4}$
			1	0.52 79$\overline{8}$	1.89 40$\overline{1}$	1.90 07$\overline{3}$	0.52 61$\overline{1}$	4.19 03$\overline{8}$	238.64$\overline{2}$
Virginium.......	Vi	**224**[1]	1	2.32 $\overline{124}$	0.43 08$\overline{0}$	8.35 $\overline{648}$	0.11 96$\overline{7}$	18.42 $\overline{288}$	54.28$\overline{0}$
Xenon..........	Xe	**131.3**	*n*	1.36 08$\overline{2}$	0.73 49$\overline{6}$	4.89 8$\overline{24}$	0.20 41$\overline{6}$	10.79 8$\overline{77}$	92.60$\overline{3}$
Ytterbium.......	Yb	**173.04**	3	0.59 772	1.67 30$\overline{2}$	2.15 17$\overline{9}$	0.46 473	4.74 38$\overline{5}$	210.797
			n	1.79 31$\overline{5}$	0.55 767	6.45 53$\overline{8}$	0.15 491	14.23 1$\overline{57}$	70.266

TABLE 99. ELECTROCHEMICAL EQUIVALENTS OF THE ELEMENTS.—
(Continued)

1	2	3		4	5.	6	7	8	9
Element	Sym-bol	Atomic weight	Val. or chg. val.	Mg./coulomb	Cou-lombs /mg.	G./ amp.-hr.	Amp.-hr. /g.	Lb./1,000 amp.-hr.	Amp.-hr. /lb.
Yttrium.........	Y	88.92	3	0.30 71$\overline{5}$	3.25 57$\overline{4}$	1.10 57$\overline{4}$	0.90 437	2.43 77$\overline{4}$	410.21$\overline{6}$
			n	0.92 145	1.08 52$\overline{5}$	3.31 72$\overline{2}$	0.30 14$\overline{6}$	7.31 3$\overline{22}$	136.73$\overline{9}$
Zinc............	Zn	65.38	2	0.33 87$\overline{6}$	2 95 1$\overline{9}$7	1.21 95$\overline{2}$	0.81 99$\overline{9}$	2.68 85$\overline{9}$	371.94$\overline{2}$
			n	0.67 75$\overline{1}$	1.47 59$\overline{9}$	2 43 90$\overline{5}$	0.41 00$\overline{0}$	5.37 71$\overline{8}$	185.97$\overline{1}$
Zirconium.......	Zr	91.22	4	0.23 63^{7}	4.23 15$\overline{3}$	0.85 07$\overline{6}$	1.17 54$\overline{2}$	1.87 5$\overline{60}$	533.1$\overline{64}$
			n	0.94 52$\overline{8}$	1.05 78$\overline{8}$	3.40 30$\overline{3}$	0.29 38$\overline{6}$	7.50 23$\overline{9}$	133.2$\overline{91}$

NOTE.—Atomic weights in bold face type indicate those in which changes have been made since the last revision of this table in 1929, or new additions to the list since that time.

Digits overscored may, if desired, be dropped from the values, rounding them off to the nearest preceding digit; such digits have been carried as a matter of convenience and uniformity in calculating and tabulating but are in excess of the number of significant figures in the primary data and hence do not add to the true accuracy of the results.

[1] Best value known; not included in the official list.

[2] This is the second isotope of hydrogen and is the only isotope included in the table, as no others have as yet been isolated to a sufficient degree to have their atomic weights determined.

[4] This value varies from the basic figure of 1.1180 mg. because of the rounding off of the value of the Faraday to 96,500 coulombs; other values also differ in the same proportion.

CONVERSION TABLES

Conversion data for mass for metric and English units are given in Tables 100 and 101, data for current density in Table 102, concentration in Table 103, linear units in Table 104, surface and area in Table 105, volume and capacity units in Table 106, heat and energy units in Table 107, of particular interest in connection with electrochemical and electrolytic computations.

TABLE 100.   CONVERSION DATA FOR METRIC AND AVOIRDUPOIS UNITS

Unit	1 Mg. per sec. → ÷	2 G. per hr. → ÷	3 Kg. per day → ÷	4 Tonnes per yr. → ÷	5 Oz. per hr. → ÷	6 Lb. per hr. → ÷	7 Lb. per day → ÷	8 Net tons per yr. → ÷	Unit
1 Milligram per sec ↑ ×	1.	3.6	0.0864	0.031557	0.12699	0.0079367	0.19048	0.034786	÷ ← Seconds per mg.
2 Grams per hr ↑ ×	0.27778	1.	0.024	0.0087658	0.035274	0.0022046	0.052911	0.0096626	÷ ← Hours per g.
3 Kilograms per day ↑ ×	11.57407	41.66667	1.	0.36524	1.46975	0.091860	2.20462	0.40261	÷ ← Days per kg.
4 Metric tons per yr ↑ ×	31.68877	114.07955	2.73791	1.	4.02404	0.25150	6.03606	1.10231	÷ ← Years per tonne
5 Ounces per hr ↑ ×	7.87487	28.34953	0.68039	0.24851	1.	0.0625	1.5	0.27393	÷ ← Hours per oz.
6 Pounds per hr ↑ ×	125.99790	453.59243	10.88622	3.97611	16.	1.	24.	4.33291	÷ ← Hours per lb.
7 Pounds per day ↑ ×	5.24991	18.89969	0.45359	0.16567	0.66667	0.041667	1.	0.18262	÷ ← Days per lb.
8 Net tons per yr ↑ ×	28.74767	103.49124	2.48379	0.90719	3.65051	0.22816	5.47582	1.	÷ ← Years per net ton
	Sec. per mg. × ↑ ←	Hr. per g. × ↑ ←	Days per kg. × ↑ ←	Yr. per tonne × ↑ ←	Hr. per oz. × ↑ ←	Hr. per lb. × ↑ ←	Days per lb. × ↑ ←	Yr. per net ton × ↑ ←	

TABLE 101. CONVERSION DATA FOR METRIC AND TROY UNITS

Unit	1 Mg. per sec. ÷	2 G. per hr. ÷	3 Kg. per day ÷	4 Tonnes per yr. ÷	5 Oz. per hr. ÷	3 Oz. per day ÷	7 1,000 oz. per yr. ÷	Unit
1 Milligram per sec. ×→	1.	3.6	0.0864	0.031557	0.11574	2.77778	1.01458	+ ← Seconds per mg.
2 Grams per hr. ×→	0.27778	1.	0.024	0.008766	0.032151	0.77162	0.28183	+ ← Hours per g.
3 Kilograms per day ×→	11.57407	41.66667	1.	0.36524	1.33941	32.15072	11.74281	+ ← Days per kg.
4 Metric tons per yr. ×→	31.68877	114.07955	2.73791	1.	3.66774	88.02578	32.15072	+ ← Years per tonne
5 Ounces per hr. ×→	8.63986	31.10359	0.74649	0.27265	1.	24.	8.76581	+ ← Hours per oz.
6 Ounces per day ×→	0.36	1.20598	0.031104	0.011360	0.041667	1.	0.365224	+ ← Days per oz.
7 1,000 oz. per yr. ×→	0.98563	3.54823	0.085157	0.031104	0.11408	2.73791	1.	+ ← Years per 1,000 oz.
	Sec. per mg. ×↑	Hr. per g. ×↑	Days per kg. ×↑	Yr. per tonne ×↑	Hr. per oz. ×↑	Days per os ×↑	Yr. per 1,000 o. ×↑	

TABLE 102. CURRENT DENSITY EQUIVALENTS

Amp/sq dm	Amp/sq ft	Amp/sq in.	Amp/sq cm
1	9.29	0.0645	0.01
0.108	1	0.007	0.00108
15 5	144	1	0.155
10	929	6.45	1

TABLE 103. CONCENTRATION EQUIVALENTS

G/l	Oz/gal	Troy oz/gal	Dwt/gal	Oz/cu ft
7.5	1	0 915	18 3	7 5
8.2	1.099	1	20	8 2
0.41	0.0549	0.05	1	0 41
1	0.134	0 122	2.44	1

TABLE 104. LINEAR MEASURE EQUIVALENTS

Kilometers, km	Meters, m	Centi-meters, cm	Millimeters, mm	Inches, in.	Feet, ft
1	1,000	10^5	10^6	39,370	3,280 83
0 001	1	100	1,000	39 37	3 28083
10^{-5}	0 01	1	10	0 3937	0 032808
10^{-6}	0 001	0 1	1	0 03937	0 0032808
$2 54 \times 10^{-5}$	0 0254	2 540	25 40005	1	0 08333
$3 048 \times 10^{-4}$	0 30480	30 480	304 801	12	1
$9 144 \times 10^{-4}$	0 914402	91 440	914 4	36	3
10^{-9}	10^{-6}	10^{-4}	10^{-2}	$3 937 \times 10^{-5}$	$3 2808 \times 10^{-6}$
10^{-12}	10^{-9}	10^{-7}	10^{-5}	$3 937 \times 10^{-8}$	$3 2808 \times 10^{-9}$

TABLE 105. SURFACE AND AREA EQUIVALENTS

Sq m	Sq in.	Sq ft	Sq yd	Sq rods
1	1,550	10 76	1.196	0 0395
0.0006452	1	0.006944	0.0007716	0 00002551
0.09290	144	1	0.1111	0.003673
0.8361	1,296	9	1	0.03306
25.29	39,204	272.25	30.25	1
404 7	627,264	4,356	484	16
4,047	6,272,640	43,560	4,840	160
2,589,998		27,878,400	3,097,600	102,400

Table 106. Volume and Capacity Equivalents

Cu in.	Cu ft	Cu yd	U.S. apoth. liquid oz	U.S. qt		U.S. gal		U.S. bu	Liters	Cc	Cu m
				Liquid	Dry	Liquid	Dry				
1	0.0_35787	0.0_42143	0.5541	0.01732	0.01488	0.004329	0.003720	0.0_34650	0.01639	16.39	1.6387×10^{-5}
1,728	1	0.03704	957.5	29.92	25.71	7.481	6.429	0.8036	28.32	28,320	0.028318
46,656	27	1	25,853	807.9	694.3	202.0	173.6	21.70	764.6	764,600	0.7646
1.805	0.001044	0.0_43868	1	0.03125	0.02686	0.007813	0.006714	0.0_38392	0.02957	29.57	2.9579×10^{-5}
57.75	0.03342	0.001238	32	1	0.8594	0.25	0.2148	0.02686	0.9464	946.4	9.4649×10^{-4}
67.20	0.03889	0.00144	37.24	1.164	1	0.2909	0.25	0.03125	1.101	1,101	11.009×10^{-4}
231	0.1337	0.004951	128	4	3.437	1	0.8594	0.1074	3.785	3,785	3.785×10^{-3}
208.8	0.1556	0.005761	148.9	4.655	4	1.164	1	0.125	4.405	4,405	4.405×10^{-3}
2,150	1.244	0.04609	1,192	37.24	32	9.309	8	1	35.24	35,240	3.524×10^{-2}
61.02	0.03531	0.001308	33.81	1.057	0.9081	0.2642	0.2270	0.02838	1	1,000	1×10^{-3}

Table 107. Heat, Energy, or Work Equivalents

Joules = 10^7 ergs	Kg-m	Ft-lb	Kwhr	Hp-hr	Liter-atm	Kg-cal	Btu	G-cal
1	0.10197	0.7376	0.0_62778	0.0_63725	0.009869	0.0_32390	0.0_39486	0.239
9.80597	1	7.233	0.0_52724	0.0_53653	0.09678	0.002344	0.0_29296	2.3438
1.356	0.1383	1	0.0_63766	0.0_650505	0.01338	0.0_33241	0.0_21286	0.3241
3.6×10^6	3.671×10^5	2.655×10^6	1	1.341	35,528	859.98	3.415	860.445
2.6845×10^6	2.7375×10^5	1.98×10^6	0.7457	1	26,494	641.7	2.545	641.659
101.33	10.333	74.73	0.0_42815	0.0_43774	41.29	0.02422	0.09612	24.218
4,183	426.9	3.086	0.001162	0.001558	1	1	3.968	999.936
1,054	107.5	778.1	0.0_32928	0.0_33930	10.40	0.25200	1	252

.

NAME INDEX

A

Abernathy, 256
Abramson, H., 150
Accumulatoren Fabrik, A.-G., 196
Acheson, E. G., 12, 635, 644, 646
Acheson Graphite Co., 710
Acker, C. E., 408, 537
Acton, England, 310
Adams, I., 9, 12
Adams, E. K., 12
Adler, E., 124
Ajax Metal Co., 592
Ajo, Ariz., 346
Alcoa, Tenn., 734
Alexander, H. H., 15
Aluminum Co. of America, 492, 502, 722, 723
Aluminum Co. of Oldbury, 398
American Bridge Co., 569
American Cyanamid Co., 617, 628, 631
American Electrochemical Society, 13
American Hard Rubber Co., 120
American Nitrogen Products Co., 682
American Smelting and Refining Co., 284, 299, 303, 329, 354, 358, 370 ·
American Zinc Co. of Illinois, 354, 359
Ampère, A. M., 19
Anaconda Copper Mining Co., 284, 348, 354, 369, 370
Anaconda Lead Products Co., 120, 122
Andes Copper Mining Co., 342, 343, 347
Andre, H. G., 179
Anthony, 9

Appelberg, A., 475
Arndt, K., 547
Arrhenius, S., 31 34, 46
Arvida, Que., 485, 721, 736
Ashley, S. E. Q., 98
Askenasy, P., 116
Aston, J., 139
Aten, A. H. W., 213, 451, 480
Atlas Powder Co., 108
Aubel, P. K., 277, 278
Aussig, Austria, 411

B

Badin, N. C., 485, 734
Baekeland, L., 14
Balbach, E., 12, 268
Balke, C. W., 550
Bancroft, W. D., 217
Basic Magnesium, Inc., 521–523
Bates, S. J., 29
Becket, F. M., 13
Bell, A. G., 9
Bengough, G. D., 256
Berry, E. R., 15
Beryllium Corporation of America, 539, 541
Bethlehem Steel Co., 375
Betts, A. G., 13, 314, 318
Bietz, 324
Billiter, J., 262, 423
Bingham, C., 614
Bird, 417
Bitterfeld, 523
Bjerrum, N., 46
Bleininger, A. V., 153, 712
Blue, R. D., 233
Blum, W., 212, 216
Boericke, F., 73
Boerlage, L., 213
Bonneville, Ore., 720, 736

753

SUBJECT INDEX

A

Abraham-Marmier ozonizer, 667

Accumulators, 184

Acids, equivalent conductivities of, 42, 43

Acker cell, 408, 537

Addition agents in copper refining, 276*ff.*

  effect of, on overvoltage, 278, 279

  in lead refining, 315

  in metal deposition, 217

  in plating baths, 229

  in tin refining, 330

Air cell, 163, 164

Ajax-Northrup furnace, 596

Ajax-Tama furnace, 594

Ajax-Wyatt furnace, 590*ff*, 593

Alkali halides, electrolysis of, 385*ff.*

  anodes for, 390

  anodic and cathodic processes in, 387

  applications of, 3, 386

  cathodes for, 390

  caustic, 385

  cells for, 400*ff.*

    classes of, 394, 396

    desirable conditions for, 395

    diaphragm cells, 412*ff.*

      with circulating electrolyte, 413

      cylindrical, 428

      submerged-cathode type, 414

  effect of temperature in, 394

  flow sheet for, diaphragm method, 388

    mercury method, 399

  German practice, 407, 408, 410

  graphite consumption in, 390, 423

  hypochlorites, 439

Alkali halides, electrolysis of, liquid chlorine from, 439

  mercury cells in, 397*ff.*

    comparison of, with other cells, 397

    history of, 397

    mercury losses in, 400

    short-circuited cathode systems in, 401

    voltage components in, 393

    moving electrolyte cells in, 411*ff.*

    operating data for, 409, 410

    salt impurities in, 392

Alkali sulfates, electrolysis of, 385

Allen-Moore cell, 421, 435

  KML type, 422

Alloys, beryllium, 544

  deposition of, 78, 246

  lead, 552

    as material of construction, 699, 702

  minor, 607

  plating of, 246*ff.*

  zirconium, 607

Aloxite, 642

Alternating current, 78

  effect of, on electrolysis, 78, 304

    on oxidizing potential, 80

  reduction of overvoltage by, 79

  superimposed, 81

    in gold refining, 304

Alumina, 401*ff.*

  application of, 3

  decomposition of, 500

  electrolysis of, 488

  flow sheet for, 484, 487

  production of, 482*ff.*

  purification processes, 482–488

  reduction of (*see* Aluminum)

  as refractory, 712